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THE DEGRADATION OF ZIRCONIUM ALLOYS IN NUCLEAR REACTORS - A REVIEW

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THE DEGRADATION OF ZIRCONIUM ALLOYS IN NUCLEAR REACTORS - A REVIEW

A review report prepared by D. Lim, N. A. Graham, and D. O. Northwood under contract to the Atomic Energy Control Board, Ottawa, Canada (Contract No. 50SS.87055-4-4049).

ABSTRACT

This report presents the findings of a survey of available non-Canadian literature on the oxidation and hydriding of zirconium alloys. Much of the literature was found to address the Zircaloys, particularly when used as fuel cladding subjected to a radioactive and oxidizing environment. Hydriding of Zircaloys is mainly attributed to oxidation. The survey revealed that Zr-Nb alloys have been included in some investigations; however, data on the long-term degradation of Zr-2.5 wt% Nb, in particular, were scarce. The reviewed literature did not lead to conclusions regarding the potential for accelerated hydriding due to corrosion at crevices and/or second-phase particles, nor did it lead to conclusions as to the potential for a "breakaway" in oxidation and hydrogen acquisition in long service life of Zr-Nb alloys. Specific information on service experience in U.S.S.R. power reactors could not be obtained; however, most of the information surveyed leads to the conclusion that fuel channels having Zr-2.5 wt% Nb pressure tubes should perform satisfactorily with respect to degradation from corrosion and hydriding provided they are installed correctly and are not operated under conditions that are far removed from those anticipated in design.

RÉSUMÉ

Le présent rapport donne les résultats d'une étude sur l'oxydation et l'hydruration des alliages de zirconium à partir des documents non Canadiens existants, dont plusieurs traitent des <<Zircaloys>>, particulièrement lorsqu'ils sont utilisés dans les gaines de combustible soumises à un milieu radioactif oxydant. On attribue principalement l'hydruration des <<Zircaloys>> à l'oxydation. La recherche a révélé que certaines études avaient inclus des expériences sur des alliages de zirconium à teneur en niobium; toutefois, les données sur la dégradation à long terme du zirconium à teneur de 2,5 % en niobium en poids, en particulier, étaient rares. L'examen de la documentation n'a mené à aucune conclusion sur la possibilité d'une accélération de l'hydruration due à la corrosion dans les crevasses ou aux particules de la deuxième phase, ou aux deux, ni sur la possibilité de hausse très rapide du taux d'oxydation et d'apport d'hydrogène dans la vie utile à long terme des alliages de zirconium à teneur en niobium. Bien qu'il ait été impossible d'obtenir des renseignements précis sur le fonctionnement des réacteurs de puissance en U.R.S.S., il reste que la plupart des renseignements examinés laissent entendre que les canaux de combustible comprenant des tubes de force à base de zirconium à teneur de 2,5 % en niobium en poids devraient

bien se comporter par rapport à la dégradation due à la corrosion et à l'hydruration, pourvu qu'ils soient installés correctement et ne soient pas utilisés dans des conditions trop éloignées des cas prévus dans la conception.

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THE DEGRADATION OF ZIRCONIUM ALLOYS IN NUCLEAR REACTORS - A REVIEW

EXECUTIVE SUMMARY

Under the general title of this project, "Degradation of Zirconium Alloys in Nuclear Reactors", the specific mission was to search and review the international literature and other information on the oxidation and hydriding of zirconium alloys in the various service conditions of nuclear power reactors. Further, particular emphasis was to be placed on the oxidation and hydriding of Zr-2.5 wt% Nb alloys under long term service conditions similar to those of CANDU pressure-tube reactors.

Much of the world zirconium literature is concerned with the Zircaloys which are used mainly as fuel cladding and, in some non-fuel applications, as flow channels. Most current applications of Zr-Nb alloys are concerned only with the Zr-1 wt% Nb and Zr-2.5 wt% Nb alloys. The Zr-1 wt% Nb alloy is used principally as fuel cladding, particularly in Russian reactors, while the stronger Zr-2.5 wt% Nb alloy has application as a structural material in the Russian pressure-tube type and CANDU reactors. Hence much of the information in the literature on the Zr-Nb alloys orginates with organizations in eastern bloc countries, those with CANDU related interests or organizations pursuing alternate alloys for the Zircaloys.

On the general phenomena of oxidation and hydriding of zirconium alloys in high temperature water systems, the general observations from the literature examined are: (i) in all environments, hydrogen pick-up rates in Zr-2.5 wt% Nb alloys are consistently lower than in the Zircaloys, (ii) oxidation rates of zirconium alloys vary with the reactor environment, since increasing oxygen content of the water enhances the corrosion rate with a decrease in hydrogen pick-up, (iii) except for some cases of localized or nodular corrosion, no evidence of accelerated corrosion accompanied by enhanced hydrogen pick-up has been reported for the Zr-2.5 wt% Nb alloys, (iv) several references were identified which reported the phenomenon of increases in oxidation and hydrogen pickup rates for Zircaloys, after long service exposures had developed oxide thicknesses greater than 12 to 15 µm, but no evidence of a similar phenomenon in Zr-Nb alloys has been identified and (v) intermetallic particles are believed to promote nodular corrosion and enhanced hydrogen pickup.

The early literature reported mainly observations from often relatively short term out-reactor corrosion tests. Later literature includes more reports on observations from longer term tests and experiences with actual service components in power reactors. No reference was found of observations from service experiences longer than those in Canadian CANDU reactors; viz Pickering A units or the older NPD unit. Much of the literature reports the phenomena observed, and sometimes offers some theory to explain the particular observations; however, there is little scientific international research effort to develop a unified theory of

oxidation and hydriding of zirconium alloys. Such a theory would be useful for explaining, and must be consistent with, the observed phenomena, such as effects of environment, material chemistry and irradiation. A well developed theory is essential for predicting material behaviour beyond what has been experienced in laboratory tests or reactor service.

There is little evidence in the literature of international research on the role of stress in the hydride cracking phenomena. Of course, interest in this field is prompted by structural applications such as those in pressure-tube reactors. The fact that this has not become a serious research topic in the published literature of the eastern bloc countries may suggest that the Russian pressure-tube reactors have not experienced hydride related problems or may have experienced problems and the findings are not satisfactory to the extent of publishing in the open literature. It is therefore recommended that every effort should be made to establish some liaison with their materials scientists to obtain updates on their experiences, particularly as their reactors accumulate operating years and unusual problems may develop.

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A. INTRODUCTION

The purpose of this investigation is to search for published and other information available in the international nuclear community on the subject of degradation of zirconium alloys in nuclear reactors which might complement information already available in the Canadian community. In particular, the specific topic to be addressed concerns the role of hydrogen (deuterium) in the degradation of Zr-2.5 wt% Nb pressure tubes, as employed in CANDU power reactors. Further, the investigation examines the sources of hydrogen, material and environment factors which affect the ingress of hydrogen into pressure tubes and other factors which affect the influence of hydrogen on the integrity of pressure tubes. Although information on Zr-Nb alloys has been emphasized, the Zircaloys have been included in the search since much of the international literature concerns these alloys.

The search has attempted to address the following specific questions, as they apply to the Zr-2.5 wt% Nb pressure tubes in CANDU power reactors:

a) Is corrosion the main agent for the zirconium hydride acquisition mechanism?

b) Do micro-alloying differences between zirconium alloys affect their respective corrosion rates?

c) To what extent does the rate of hydrogen pickup depend on the hydrogen concentration in the material?

d) Is delayed hydride cracking due to high stress levels, low temperature gradients and/or other factors?

B. METHODOLOGY

A search of the basic research and R&D reports of non-Canadian sources on the degradation of zirconium alloys in nuclear environments was made by computerized searches of international databases and libraries and the establishment of contacts with foreign nuclear establishments and researchers involved in working with zirconium alloys.

The majority of the database searches was performed through DIALOG (database service) from the University of Windsor and some searches were done on the CAN/OLE system of CISTI (Canadian Institute for Scientific and Technical Information) from Westinghouse in Port Hope and on the DIALOG service from the Westinghouse R&D Centre in Pittsburgh. Relevant non-Canadian articles were obtained from the following databases searched: INIS (International Nuclear Information System), NTIS (National Technical Information Services), EPD (EPRI - Electric Power Database), METADEX (Metals Index), EI (Engineering Index), DOE (Department of Energy files #103 and #104), Library of Congress, EIM (Engineering Meetings) and WTEC (Westinghouse database). These databases were chosen because they are considered to provide a comprehensive coverage of the international and North American work on the technology of zirconium and its alloys. The suggestions through correspondence with the libraries at EPRI, UKAEA and ORNL was to search through some of the databases mentioned above. Among the keywords used for the searches were zirconium, hydride, Zircaloy, niobium, columbium, alloys, Zr, hydrogen, corrosion, crack, embrittle.

A lot of duplicate hits were obtained among the various databases. The major sources for the articles obtained were the INIS, METADEX, and NTIS databases. The INIS is the database produced by the International Atomic Energy Agency which is composed of over 50 countries and international agencies. The database covers all aspects of peaceful applications of atomic energy and monitors journals, theses and conference proceedings. METADEX provides a comprehensive coverage of the international literature on the science and technology of metals including applications, forms, materials, processes, products and properties. Over 1200 journals are monitored as well as books, conference proceedings and theses. The NTIS database represents US Government sponsored research, development and engineering reports which originate from over 300 US Government departments and agencies eg. NASA, Department of Defence, and Department of Energy. The database covers science, technology, education and also includes some government sponsored translation, foreign language reports and information on US Government patents.

Besides the database searches, foreign nuclear research and development bodies were contacted to assist in the location and acquiring of relevant reports. Individual persons or establishments in the following countries were contacted in this pursuit: Australia, Argentina, Brazil, China, Czechoslovakia, Denmark, Finland, India, Japan, USSR, UK, Norway, USA, Taiwan, Sweden, Germany and Pakistan. A list of these people and institutions is included in Appendix A. Responses were received from all countries with the exception of Brazil and Pakistan. A number of reports were obtained from some of these sources through the co-operative efforts of those individuals involved. Some of our requests for information and reports were refused due to the proprietary nature of these information to establishments particularly in Sweden, Finland and Czechoslovakia.

Personal contacts were also made through attendance at recent international conferences dealing with corrosion, hydrogen and zirconium to determine any major concerns within the nuclear community pertaining to the essence of this program. The three conferences attended were: 1) Asian Pacific Corrosion Control Conference in Tokyo, 2) Hydrogen in Metals Conference in Belfast and 3) 7th ASTM Conference on Zirconium in the Nuclear Industry in Strasbourg.

A trip was made by one of the authors (D. O. Northwood) to the Power Reactor and Nuclear Fuel Development Corporation (PNC) in Japan to investigate the pressure tube research program for the Fugen reactor. Some early out-reactor and recent in-reactor corrosion/hydriding test results of Fugen pressure tube material has been promised when they become available later this year. PNC has confidence in the performance of the heat-treated Zr-2.5 wt% Nb pressure tubes as they have no concern with high hydrogen pickups since their out-reactor tests give them confidence that hydrogen pickups would be small.

Besides mentioning that they are currently doing some corrosion tests on welds of Zr-2.5 wt% Nb shroud tubes, the Finns would not comment on the corrosion behaviour of the alloy since they consider it to be Russian proprietary information.

Attempts to establish contact with USSR institutions were unsuccessful probably because it required the approval of their State Committee on the Utilization of Atomic Energy for responses to our letters.

C. SOURCES OF HYDRIDE IN PRESSURE TUBES

The principal question covered in this section of the literature review is: Is the water side corrosion reaction the principal source of hydride in CANDU pressure tubes? In the context, the principal sources considered are the corrosion reaction with the water coolant on the internal surface, the insulating gas annulus on the outer surface and any end-effect or influence at the endfitting rolled joint.

Much of the research and development work performed outside Canada on the oxidation and hydriding of zirconium alloys has been on the Zircaloys and their application in PWR* and BWR** coolant environments. The Russian reactors use two types of Zr-Nb alloys: the Zr-1 wt% Nb alloy as fuel cladding and the Zr-2.5 wt% Nb alloy as structural pressure tubes in their graphite-moderated reactors. The literature obtained on Russian operating experience and research investigations with these alloys are generally vague and often contain little elaboration. There is a reasonable body of data but it is poorly or inadequately reported.

Zirconium alloys in a nuclear reactor environment are subjected to a complex interaction of many variables which affect the oxidation and hydrogen pickup processes. On the water side, it is generally accepted that the source of hydrogen is from the basic zirconium-water corrosion reaction $Zr + 2\,H_2O \rightarrow ZrO_2 + 2H_2$. The degree of hydrogen pickup in the metal from this reaction depends on environment and material variables which include coolant chemistry, alloy chemistry, metallurgical and surface conditions, the thickness of oxide acquired and neutron flux. On the insulating gas annulus side, hydriding sources may be from contaminants such as water, other hydrogenous species and hydrogen itself; hydrogen pickup from these sources depends on the contamination level and the oxidation-reduction potential of the environment relative to zirconium. The role of a dissimilar metal endfitting on hydriding depends on the material (AISI 403 stainless steel in the CANDU) and the nature of the attachment. Potential hydriding influences that can be considered at the endfitting include galvanic effects on the corrosion reactions on the adjacent pressure tube, a hydrogen 'window' effect at areas of metal bonding and local crevice environment effects.

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* Pressurized Water Reactor

** Boiling Water Reactor

1. Aqueous Corrosion in BWR Environment

Coolant water undergoes radiolytic decomposition in the strong radiation field of the reactor core giving rise to small amounts of hydrogen and oxygen dissolved in the water and in addition a series of short-lived radicals. In a BWR environment, the hydrogen and oxygen in the water phase never reach equilibrium and consequently the BWR operates with appreciable amounts of hydrogen and oxygen in the water and steam phases; $\geq$ 0.05 ppm O_2 in the water phase and about 10 ppm in the steam phase(1). Due to the simultaneous presence of hydrogen and oxygen, the water can be both reducing and oxidizing with the latter property being more apparent leading to an increased corrosion rate and a reduced hydrogen pickup. There are no additives in the BWR coolant and these reactors normally would operate with a pure water chemistry under "oxidizing" water conditions due to the presence of dissolved oxygen.

In the BWR water, the effects of oxygen will dominate leading to a low hydrogen pickup ratio. The hydrogen uptake of Zircaloy-2 in BWRs do not normally exceed 10% of the stoichiometric equivalent of the corrosion reaction and may be as low as 3%. In the Advanced Test Reactor (ATR) test loop, the hydrogen pickup was normally below 6% in oxygenated water containing 0.6 ppm O_2 (2). In low oxygen water ($<$ 0.05 ppm O_2) in the same loop, the pickup ratio reached 44%. There is hardly any evidence for a difference in hydrogen pickup behaviour between Zircaloy-2 and -4 in oxygenated BWR water.

Garzarolli et al(3) performed post-irradiation measurements of oxide layers and hydrogen contents of Zircaloy-2 cladding of fuel elements of German BWR reactors (VAK, KWL, KRB, see Table I) which had been in operation for 1 to 7 years. The hydrogen pickup is only 3-7% of the stoichiometric value and the net hydrogen content of the claddings (0.9 mm wall thickness) was less than 100 ppm after 7 years of operation. The hydrogen pickup seems to depend on the oxide layer thickness and is locally higher at spots with spalled oxides. No values were reported for the amount of hydrogen in these regions. Investigations of isothermal corrosion samples of Zircaloy-2, -4, Zr-2.5 wt% Nb and Zr-3 wt% Nb-1 wt% Sn after 1 year exposure (at 285°C) showed that the corrosion behaviour of Zircaloy-4 is similar to Zircaloy-2 and that Zr-2.5 wt% Nb has a higher in-pile corrosion rate than the other alloys. Figure 1 shows the trend for Zircaloy-2 fuel cladding corrosion. The corrosion behaviour of all the alloys lie within the band except for Zr-2.5 wt% Nb which shows a definitely higher corrosion rate in this short duration test. The absorption of corrosion hydrogen in the Zr-2.5 wt% Nb and Zr-3 wt% Nb-1 wt% Sn was 4%, a little lower than that of Zircaloy-2 fuel clad (~ 5%).

Figure 2 shows the weight gain and the hydrogen content along a VAK element after 920 days irradiation. The weight gain from oxidation and hydrogen content both seem to be highest at the peak heat flux location of the fuel rod(3). The weight gain and the hydrogen pickup data of fuel elements from a series of BWRs are plotted in Figures 3 and 4. In spite of the different water chemistry and heat flux of the BWRs, all the fuel elements show a similar corrosion behaviour except for the first-core fuel elements of the VAK. No explanation was given for this remarkably higher corrosion rate. The hydrogen pickup rate of BWR Zircaloy fuel cladding is generally similar for all different reactors, Figure 4.

Three types of oxide layers are observed on Zircaloy fuel rods by Garzarolli et al(4) in BWRs. The normal type of oxide layer is a thin uniform layer which does not exceed 15 µm even after 10 years of exposure. In addition to this uniform oxide layer, a nodular type of oxide has been observed. Oxide nodules up to 250 µm have been seen after long time exposure (no duration given) with no indications of spalling in spite of the fact that oxide breakaway or spalling occurs normally at 70 µm. The third type of oxide observed is an increased uniform layer which grows uniformly in thickness up to about 70 µm before spalling starts to occur. No analysis was reported by the authors to determine any relationship between hydrogen pickup and the various thicknesses of oxides observed, since normal uniform corrosion or increased normal corrosion in BWRs is usually of minor concern in service. The formation of nodules can become quite significant, particularly after long exposures which affects primarily the wall thinning of the cladding.

Sheppard and Tyzack(5) of the UKAEA (United Kingdom Atomic Energy Authority) in UK investigated the corrosion behaviour of Zircaloy-2, -4 and Zr-2.5 wt% Nb pressure tubes in the Steam Generating Heavy Water Reactor (SGHWR) for exposures up to 531 days. The inlet water of the reactor typically contains 0.07 - 0.10 ppm of oxygen. The hydrogen pickup results show considerable scatter and appear to be largely independent of corrosion weight gain. The pickup values were mostly below 5 percent. However exceptions are Zircaloy-2 pressure tubes which had been quenched and fabricated or preoxidized at 450°C for 14 days. These specimens showed much greater pickup ranging from 10 - 30 percent. The hydrogen pickup seems to be largely independent of weight gain, making the percent pickup data of uncertain value. The authors implied that the process promoting hydrogen pickup is independent of that involved in increased corrosion in-reactor. Based upon the worst case results, a Zircaloy-2 tube could be expected to attain a maximum oxide thickness of ~ 800 µm and an increase in hydrogen content of only 37 ppm for an assumed reactor life of 200,000 h. From these extropolated results, Sheppard and Tyzack stated that neither the loss of section by corrosion nor hydrogen pickup by the pressure tube should be life-limiting.

Castaldelli et al(6) studied the corrosion behaviour of zirconium alloys in the Halden Boiling Water Reactor (HBWR) under water chemistry typical for a BWR with an oxygen content of 0.03 ppm. Zircaloy-2 was observed to have a hydrogen pickup of about twice that of niobium containing alloys and niobium additions was found to be beneficial in preventing hydrogen pickup, Figure 5.

Videm(7) in a review paper on the corrosion and hydrogen pickup of zirconium alloys, stated that the hydrogen uptake of Zircaloy-2 does not normally exceed 20% of the stoichiometric equivalent of the corrosion and may be as low as 5% because of the oxidizing potential of the water in BWR reactors which tend to promote a reduced hydrogen pickup. These values were later revised to 10% and 3% respectively in a later paper(1) by the same author.

Zaimovskii(8) mentioned that with respect to the corrosion of Zr-1 wt% Nb fuel element cladding, it is in the "boiling reactor RBMK*" that the most severe conditions are created. Citing corrosion results from co-workers at the Kurchatov Atomic Energy Institute, USSR, for Zr-1 wt% Nb and Zr-2.5 wt% Nb alloys under conditions of boiling non-corrected water in the RBMK reactor for times up to 20,000 hours, it was found that both these alloys are "fully corrosion resistant". Focal (localized) corrosion similar to that on Zircaloy was observed on the Zr-1 wt% Nb alloy up to depths of ~ 100 µm. No corresponding hydrogen pickup values were given.

Referring to the reliability of VVER** and RBMK type (Zr-1 wt% Nb) fuels, Solyany et al(9) stated that even after long-term irradiation (no time period given) under conditions of both VVER and RBMK, the hydrogen content does not exceed 100 - 200 ppm. The hydrides are initially oriented either in chaotic or circular manner. When "corrosion centres" (assume localized corrosion) appear at the areas adjacent to hydrides, the latter arrange radially.

Tsykanov et al(10) examined the corrosion behaviour of Zr-Nb alloys in the VK-50 reactor. Table II shows the water chemistry of the coolant of the reactor with the amount of oxygen ranging from 0.0025 - 0.250 ppm. During the first 5.2 years of operation of the fuel elements, the water chemistry was neutral uncorrected; then a neutral oxygen cycle was introduced after which the water-chemical indices of the coolant was markedly improved (reduced crud formation). After 8 years exposure, the Zr-2.5 wt% Nb tubes were covered with uniform thickness of oxide film on the internal and external surfaces and a maximum thickness of up to 200 µm at the fins (no reference given as to what and where these fins were) was observed. The Zr-1 wt% Nb fuel cladding was observed to undergo a predominantly continuous rate of corrosion during the initial stage until an oxide film thickness of 50 µm is attained. In the next stage, an acceleration of localized corrosion developed after which a stage of gradual increase in thickness occurred with approximately the same rate as the first stage. Figure 6 shows the maximum oxide film thickness developed versus the in-reactor time. The hydrogen content varied along the fuel element cladding and ranged from 130 - 500 ppm after 6 years operation and 240 - 730 ppm after 8 years operation. The fuel element cladding in the middle sections of the active zone were subjected to the maximum hydrogen pickup and those in the upper section to the minimum pickup. A similar trend occurred for the thickness of deposits found on the fuel cladding, Figure 7. These deposits (in our opinion) may probably include crud accumulation of oxides of iron, copper and manganese. No hydrogen analysis was given for the Zr-2.5 wt% Nb alloy which would normally have a lower pickup than Zr-1 wt% Nb(11).

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* Light water-cooled, graphite-moderated channel type reactor containing Zr-2.5 wt% Nb pressure tubes

** Pressure vessel water reactor (Russian PWR)

A localized form of corrosion which is commonly observed in boiling water environments is known as nodular corrosion. This form of corrosion is rather similar to pitting, appearing as local formation of white circular oxide patches of 0.2 - 0.5 mm diameter. The term 'nodule' is used to describe the local thickening of the oxide which appear as an eruption and having depths of attack which often vary in the range of 10 - 200 µm. As the nodules multiply and spread, coalescence occurs to give complete coverage of larger areas with white oxide. This corrosion phenomenon has also been described at times as "pustules", "pimples", "speckles" or "lenses".

Trowse et al(12) reported that in the SGHWR, nodular corrosion is the dominant form of attack on Zircaloy as it is in other boiling or oxygenated reactor environments. Extensive nodular corrosion have been observed opposite grid positions both on the tube and on the braze heat-affected zone at the spacer pad positions in the SGHWR reactor(5). This led to the belief that nodule formation may be associated in some way with disturbances to coolant flow in the vicinity of grids under boiling oxygenated conditions. Another observation is that the nodules are first formed when the oxide growth has reached the post-transition region, and Trowse(13) has drawn attention to the fact that it is observed under conditions where the uniform corrosion is considerably enhanced, as under the combined influences of oxygenated conditions and neutron flux. Recrystallized Zr-2.5 wt% Nb in two fuel elements showed more resistance to nodular corrosion than Zircaloy-2 in similar tests. No significant nodule formation was observed in the former alloy. Pickman et al(14) in a review of Zircaloy performance in water reactors stated that considering the behaviour of zirconium alloys under BWR conditions, Nb containing alloys (> 0.5%) are the best overall for corrosion resistance.

Localized corrosion and non-uniform oxide formation however has been observed on both the Zr-1 wt% Nb and Zr-2.5 wt% Nb alloys in the Soviet VK-50 reactor(10). Tsykanov et al(10) attributed the formation of the thick oxide film found on the fin region of Zr-2.5 wt% Nb sheath tube (mentioned previously) to a residual stress enhanced corrosion. This region could possibly be in or near the heat-affected zone of welded components (this is just our guess). Localized corrosion in Zr-1 wt% Nb cladding is observed after prolonged testing (3.5 years) in the reactor. While the average oxide thickness of the cladding is 5 - 7 µm, there are areas where the thickness of the film is approximately 60 µm. The hydrogen content of the cladding did not exceed 100 ppm after 3.5 years reactor operation.

In reviewing the corrosion problems associated with the fuel elements in the Soviet VVER type of reactor, Vrtilkova et al(15), stated that local (nodular) corrosion does occur in Zr-Nb alloys. This is evidenced by oxide spalling caused by the effect of neutron flux (at high oxygen concentration in the coolant) on the fuel cladding as well as "casings of the cassettes" which are made from Zr-2.5 wt% Nb. If the neutron flux is doubled, nodular corrosion can increase by a factor of five.

Trowse(13) reports that a better correlation is obtained when the nodule thickness is compared to burnup rather than time indicating that there might be a dependence of nodule distribution on the flux level. Such relationships were also indicative of observation in German reactors. Garzarolli(16) found that the depth of the local attack along the fuel pins followed the flux profile. It is also possible that a critical flux level has to be exceeded before the nodules will start to form.

Sheppard and Tyzack(5) suggested that the nodular corrosion observed in Zircaloy in-reactor in oxygenated water is due to a localized cathodic depolarization process probably involving, at least initially, electron transport through partially oxidized intermetallic particles and the reaction with oxygen containing radicals in the coolant. It is suggested that there are certain areas in the oxide film where the normal rate determining processes in film growth can be short circuited under conditions where more reactive oxygen atoms or oxygen containing radicals are available. These preferentially conducting electronic sites are associated with impurities and intermetallics lodged in the oxides which provide anodically active sites and short circuit path for the electrons. An alternative cathodic reaction can then occur locally causing the cathodic depolarization of the activated oxygen atoms produced by radiolysis. Together with the stress-induced recrystallization of the oxide, these two processes are specifically responsible for nodule initiation and growth(12). As suggested in Shirvington's work(17) the oxide nucleated in these circumstances is porous and water permeable and this would tend to promote accelerated attack with solution or surface diffusion transport of ions as opposed to solid state diffusion which would be slower at these temperatures.

Observations on hydrogen pickup on material covering the full range from absence of nodules to maximum patch thickness as reported by Sheppard and Tyzack(5) show that for increases in the oxide thickness of between 10 and 20 times the corresponding range of hydrogen pickup are only increased by 1.5 and 3 times.

There are strong indications that the tendency to form nodules in Zircaloy-2 is at least partially linked to the size distribution of the intermetallic particles(18). A structure containing coarse second phase particles seems to be particularly susceptible whilst a fine dispersion of second phase particles seems to be a prerequisite for good resistance to nodular corrosion. By beta quenching, a particle refinement is obtained, which drastically improves the nodular corrosion. This treatment has the effect of reducing the volume fraction and mean particle size of the intermetallic particles and increasing their number density in the Zircaloy.

Cheng and Adamson(19) studied the nucleation and growth behaviour of the nodular oxide and found that the site for nucleation was not at large precipitates but at locations free of precipitate. A nodular corrosion mechanism is proposed based on the local solute depletion and its effects on the stoichiometric structure of the initial black oxide. It is the inability of a localized near-stoichiometric oxide to grow while adjacent to stoichiometric oxide that is considered to lead to localized breakdown of the protective oxide and the formation of a granular type, highly porous, non-protective nodular oxide.

Kuwae et al(20) propose a mechanism for nodular corrosion which proceeds with the dissociation of the water molecule H_2O on the surface of the initial black film, Figure 8. The oxygen anions diffuse inwards while the hydrogen protons remain on the surface. Zirconium oxide and electrons are produced at the oxide-metal interface. Due to the low electrical conductivity for the usual Zircaloy oxide film, the protons migrate in preference to the conduction of electrons through the oxide to react with the electrons to produce hydrogen molecules. When the pressure of the H_2 gas accumulated at critical points on the interface exceeds the pressure the ZrO_2 film can withstand, the protective film is broken. Once this film breaks it is difficult to repair and direct access of H_2O to the matrix initiates the nodular type of corrosion. The influence of heat-treatment on the corrosion resistance of Zircaloy is attributed to the particle distribution. Beta quenching the Zircaloy induces chain-like second phase particles which retain the electrical conductivity in the ZrO_2 film throughout the whole surface. Electron conduction occurs preferentially through the oxide resulting in H_2 gas formation which takes place principally on the surface of the ZrO_2 film and prevents nodular corrosion from occurring.

Figure 9 shows the nodular corrosion results of Kuwae et al on Zircaloy-4 (α-annealed at 873 K for 2 h, air cooled) in 10.5 MPa steam at 773 K. The oxygen content of the matrix is almost constant during the corrosion while on the other hand, the hydrogen content in the matrix increased signficantly with time, in agreement with the corrosion weight gain. The hydrogen absorption ratio during nodular corrosion was about 20 percent. These values however should be used with caution since the tests were conducted out of pile in autoclaves with unknown hydrogen overpressures.

In summary, the corrosion of zirconium alloys is enhanced in the oxygenated coolant conditions of the BWRs. No cases of severe hydrogen pickup have been reported as a result of corrosion (uniform or nodular) except for the Soviet Zr-1 wt% Nb fuel cladding after long exposures. No signficant studies have been performed on hydrogen pickup of zirconium alloys in BWRs because hydrogen content values obtained in service have been normally within the design limits. Data from the Soviet experience with Zr-Nb alloys in their reactors is even more limited than data for the Zircaloys.

Regarding nodular corrosion, the mechanism of this form of attack is not yet fully understood. Differences between the hypotheses of Kuwae and that proposed by Sheppard and Trowse indicate that hydrogen pickup should increase in the former case while there should be no major changes in the latter. In-reactor work by the latter authors show no significant increase in pickup due to nodular corrosion while Kuwae's hypothesis has yet to be proven with in-reactor evidence.

The nodular corrosion of Zr-Nb alloys has not been systematically studied since it is the general belief that the alloy is less sensitive to this form of corrosion primarily due to the absence of intermetallic inclusions and having a more protective tenacious oxide film. The Soviet's long term in-reactor exposure have indicated that thick oxides and high hydrogen buildup in Zr-1 wt% Nb alloys can occur. A significant observation is of the hydrides reorienting in a radial direction around the nodules which can be detrimental in pressure tube applications. Since Zr-Nb alloys can have a second phase in the alloy, the latters role in the influence of long term corrosion and hydrogen pickup should be thoroughly investigated.

2. Aqueous Corrosion in PWR Environment

The hydrogen uptake (pickup fraction) by zirconium alloys during aqueous corrosion in PWR is mainly influenced by the alloying elements and by the chemical composition of the water. The majority of the corrosion data reported assumes that the primary source of hydrogen is via the water-metal corrosion reaction.

In the PWR coolant, water additives like LiOH or KOH are added to reduce corrosion product transport and activation and the general corrosion of reactor system components. The radiolytic oxygen produced by the decomposition of water in the radiation field of the reactor core is forced to a low equilibrium level by the addition of hydrogen or ammonia to the coolant. As hydrogen chemically is a reducing agent, the PWR water conditions are designated "reducing" in contrast to BWR water, which is "oxidizing" due to the presence of oxygen.

The pickup fraction of Zircaloy-2 depends on the oxygen content of the water and is mostly between 10 and 50%. Videm(7) (quoting from Canadian work) stated that if too high a hydrogen concentration is used, the hydrogen pickup rises to much higher values, even above 100%. Zircaloy-4 has a pickup fraction between 5 and 20% while for Zr-2.5 wt% Nb alloy it is usually smaller than 5%(21).

Deliberate or inadvertent increases in oxygen content of the reactor coolant produce pronounced enhancement of the corrosion rate of Zircaloy. The effect of oxygen (up to 0.3 ppm) in the primary coolant was demonstrated in the first cycle of operation in the German Kernkraftwerk Obrigheim reactor (KWO) during which oxide films up to 80 µm were found after 512 days at power. The oxygen content was then reduced to an average of 0.04 ppm for the second and third cycles which resulted in an oxide layer of 16 µm after similar exposure(4).

Johnson et al(2) also demonstrated the influence of dissolved oxygen in the primary coolant on Zircaloy corrosion behaviour in the loop of the Advanced Test Reactor (ATR) sited at the National Reactor Testing Station, Idaho. The loop coolant was demineralized water maintained at pH 10 ± 0.2 (room temperature values) by the addition of LiOH. For the oxygenated run, the dissolved oxygen in the loop coolant was maintained at a mean value of 0.6 ppm while for subsequent deoxygenated runs hydrazine and hydrogen were added to control the oxygen below 0.05 ppm. In the deoxygenated water, Zircaloy corrosion behaviour paralleled the out-reactor behaviour (out-reactor data extrapolated to 102 d for comparison from data points at < 65 days) while in the oxygenated test, the corrosion rates of Zircaloy specimens located at high flux positions (~ 9.5 X 10^{20}n/cm^2) were substantially accelerated over both out-reactor corrosion rates as well as corrosion rates measured on Zircaloy specimens located at lower flux positions (~ 3.4 X 10^{19}n/cm^2). In the latter position as-etched Zircaloy had weight gains approximately equal to corresponding unirradiated controls.

From a review on external corrosion of cladding in PWRs Stehle et al(21) stated that with zirconium-niobium alloys increasing oxygen content in the coolant increases corrosion with or without neutron irradiation. Quoting a Canadian source, the authors indicated that Zircaloy-2 is not influenced by changes in the oxygen content in water at 288°C without neutron flux, whereas Zr-2.5 wt% Nb is strongly influenced.

Oxygen has been observed to promote the formation of pustules on Zr-2.5 wt% Nb at high flux locations in VVER reactors(15) and in the Engineering Test Reactor (ETR) and ATR environments(22). The ETR is an older loop which ran on cycles containing dissolved oxygen concentrations of ~ 1 ppm and 0.05 ppm. All high flux Zr-2.5 wt% Nb specimens developed similar spots (pustules at the centre of gray oxide spots) regardless of surface and metallurgical conditions in oxygenated water. Electron microprobe analysis of a specimen showed no significant evidence of niobium segregation which could serve as centres for pustule formation. However major chromium segregation was observed at pustules in the oxide on Zr-Cr-Fe specimens. The percentage of corrosion hydrogen absorbed was lowest (3 to 14 percent) for the Zr-2.5 wt% Nb alloys whilst the percentages were remarkably high (sometimes > 100 percent) for Zr-Cr-Fe specimens. For Zircaloy-2 these values ranged from 19 to 43 percent. Johnson(22) observed that Zr-2.5 wt% Nb has consistently shown the highest resistance to hydriding. The annealed, cold-worked condition had high corrosion rates in the oxygenated coolant, but the percentage of hydrogen absorbed was low being in the range of values also obtained for the quenched, cold-worked and aged condition. Johnson concluded that for Zr-2.5 wt% Nb alloy, hydrogen absorption was relatively insensitive to environment.

The transfer of Zircaloy coupons from oxygenated to the deoxygenated tests in the ATR gave results different from those obtained in a similar test sequence in the ETR. In the ETR G-7 loop experiments, specimens transferred from oxygenated to deoxygenated conditions continued to oxidize at the high rates established in the oxygenated media after the transfer(2) while in the ATR tests, corrosion rates appeared to decrease gradually. However, the oxide thickness on the ETR specimens at the time of transfer were much thicker at 460 - 740 mg/dm^2 (30 - 48 µm calculated) compared to 125 - 160 mg/dm^2 (8 - 10 µm calculated) for the ATR specimens.

Besides being affected by the oxygen content of the coolant, the corrosion of zirconium alloy is also influenced by the fast neutron flux which can enhance the corrosion rate by radiation damage and radiolytic effects. Asher and Kirstein(23) found that in oxygenated water (~ 0.2 ppm O_2) only part of the in-reactor enhancement persists during post-irradiation of Zircaloy samples which were removed from the reactor. The authors attributed the in-reactor enhancement to radiation damage effects (which persist for sometime after removal from radiation source) and partly due to the effects of radiolysis which disappeared almost instantaneously. Examination of high flux specimens by Johnson(24) indicated a radiation induced nucleation of localized oxide breakdown. This nucleation was considered to be an important factor in the accelerating mechanism on high flux Zr-Cr-Fe and Zr-2.5 wt% Nb specimens. The absence of non-uniform attack on low flux and out-of-flux Zr-2.5 wt% Nb specimens indicates that some minimum level of flux or fluence is required to nucleate the non-uniform attack. The consequences of this flux related nucleation were only observed to become significant at a fast fluence of 1.7 X 10^{21}n/cm^2. In-flux hydriding rates followed the general trend of in-flux corrosion rates. The percent hydrogen pickup did not change significantly with the increase in corrosion rate observed in the 174 day test. A general conclusion made by Johnson then is that the flux appears to accelerate hydriding by enhancing the corrosion rate and not by affecting the mechanism of hydrogen pickup.

In the KWO (German PWR) mentioned above, the formation of thick oxide layers, which consisted of a relatively thin dense uniform film next to the Zircaloy and a porous circumferentially cracked upper layer, was observed after the first (oxygenated) cycle(25). Nodular corrosion was observed on some cladding, as well as partial spalling of the oxide layer. Figure 10 shows the corrosion behaviour of these first cycle rods. It is evident from this figure that the oxide layer growth in an oxygenated environment is strongly dependent on the rod local power, i.e. the thickest oxide layers were found at the high power section of the rods. The KWO was subsequently operated under reducing conditions consisting of 2 - 4 ppm H_2 overpressure and only 0.01 - 0.02 ppm O_2. The oxide layer growth under this "normal" PWR operation (reducing environment) is shown to be strongly temperature dependent, Figure 10. Figure 11 shows a typical trace of the oxide layer thickness along a PWR fuel rod. The spacer grid regions are chacterized by reduction in corrosion attributed to lower local temperature caused by an increase in both coolant velocity and local turbulence as well as a local depression in power within the grids.

Examination of Zircaloy-2 fuel cladding in the PWR at Shippingport Atomic Power Station after 4100 days by Hillner(26) showed only the anticipated uniform post-transition corrosion products with no evidence of gross Zircaloy corrosion acceleration. The oxide films were tightly adherent to the cladding and had a thickness range of 7 - 12 µm. These oxide thicknesses were about 2.4 times larger than predicted. Hillner assumed that the discrepancy between measured and predicted oxide film thickness, was due to the enhanced corrosion associated with the fast neutron irradiation exposure, even in the presence of a highly reducing environment. The accelerated corrosion attack was however accompanied by a much lower total hydrogen pickup. Approximately 65% is anticipated for the Zircaloy-2 in that region of post-transition kinetics whereas an average pickup of ~ 28% was noted. The PWR was maintained at hydrogen concentrations in the range of 10 - 63 cc H_2/kg H_2O during its operation. Other assumptions by Hillner (though not readily apparent) for the accelerated corrosion is the possibility to retain localized oxidizing conditions in the hydrogenated PWR coolant for longer periods of time (after the addition and adjustment of makeup water containing < 0.14 ppm oxygen). It is also conceivable that for prolonged exposures even minor increases in the residual oxygen content in the coolant can accelerate corrosion with reduced hydrogen absorption as observed in the Zircaloy-2 rods.

Further examination of fuel rods from the same reactor after ~ 6300 days again showed no evidence of unexpected corrosion deterioration(27). The corrosion films were tightly adherent to the underlying cladding. These claddings represent the longest continuous in-reactor exposure of Zircaloy achieved to date with a significant portion of the corrosion spent in the post-transition oxidation regime. Figure 12 shows the hydrogen distribution along the fuel rod as a function of fast fluence. There is an increase in hydrogen pickup with increasing fluence particularly within the mid region of the rod during corrosion in the post-transition regime. Figure 13 shows our replot of all the data from the Shippingport PWR fuel rod examinations reported by Hillner(26,27). At oxide thicknesses between 10 - 12 µm there is a sharp increase in hydrogen content with no corresponding increase in oxide thickness. At approximately 16 µm of oxide thickness, a sharp increase in hydrogen content occurs. The author also observed that the hydrogen pickup per unit weight gain is 2 -3 times greater in the late post-transition period (6300 days) than that observed in the early post-transition region (4100 days).

Recently Babcock and Wilcox reported the examination of fuel assembly from the Duke Power Oconee reactor after 5 cycles (50.6 GWd/tU)(28) in a study of the integrity of PWR fuel at high burnup. Hydrogen pickup was reported to increase dramatically in the fifth cycle and the rate of oxide growth also accelerated, although there were no indications of any cracking or flaking of the oxide layer. No quantitative data was given by this source. These increased hydrogen pickup phenomena may be due to the thick-film effect as hypothesized by Johnson(29), which indicated that the oxides of Zircaloy on reaching approximately 12 µm under reactor irradiation, will tend to isolate the metal/oxide reaction interface from the coolant and subsequently the oxidation rate increases due to radiolytic processes within the oxide. The combination of a thick oxide and a hydrogen rich coolant accelerates the hydrogen absorption probably due to the increases in porosity of the barrier layer which enhances hydrogen permeation. The percent hydrogen pickup of a Hanford N-Reactor Zircaloy-2 pressure tube after 3203 days reached up to approximately 100%, but in most cases was within 50 - 60%(29), while the Shippingport fuel clad had pickups ranging from 47 - 54%.

With regards to thick oxide films, Johnson(29) also observed that in-flux oxidation rates were high on Zircaloy-2 specimens which were prefilmed in an autoclave at 400°C, 9.9 MPa steam to form oxides > 13 µm and subsequently exposed in a low oxygen coolant. The corrosion rates varied substantially for each alloy as a function of prefilm treatment. Generally the corrosion rates were lowest for Zr-2.5 wt% Nb, intermediate for Zircaloy-2 and highest for Zr-Cr-Fe. As-etched Zr-2.5 wt% Nb and Zr-3 wt% Nb-1 wt% Sn specimens were reported to have higher weight gains than the corresponding prefilmed specimens(24). No reason was given for this behaviour.

Stehle et al (21) also reported that it was observed in several experiments, that pre-oxidation of the fuel tubes accelerated the corrosion rate under typical PWR water conditions probably due to the memory effect resulting from the higher pre-oxidation temperature. No references were given by the author on these cases.

Lunde and Videm(30) studied the behaviour of pickled, autoclaved and anodized Zircaloy-2 in the Halden Boiling Water Reactor (HBWR) at 240°C. Under normal conditions, the different surface treatments were observed to only affect the corrosion rate for a short period. After about 100 days exposure both fuel pins and Zircaloy samples corroded at about the same rate.

Videm(7) also reported in a review paper that under most conditions and after some exposure (no duration given), Zircaloy-2 and -4 exhibit about the same corrosion rate in the autoclaved and pickled conditions. It is also reported that autoclaving significantly increases the in-pile corrosion rate of Zircaloy-2 with larger effects after autoclaving at 400°C than at 300°C, increasing with increasing pressure.

Another form of accelerated corrosion which may occur in the PWR environment is crevice corrosion where active species are concentrated in the crevice. Isothermal laboratory corrosion experiments conducted by Cohen and others(31) have shown that the corrosion rate of zirconium alloys is not accelerated in the presence of lithium hydroxide provided the pH of the coolant remains below about 11.3 However the lithium hydroxide concentration can increase locally under high heat-transfer conditions and/or between surfaces in intimate contact.

In ATR tests with lithiated non-boiling water of pH 10, Johnson et al(2) observed thicker oxide in crevices between corrosion coupons and Zircaloy washers. A crevice corrosion mechanism may have been operating there, in which the crevice consumed water during normal oxidation, causing LiOH to concentrate in the water remaining in the crevice resulting in a sharp increase in the corrosion rate. Crevice corrosion can also be manifested by lithium hydroxide solution concentrating in the very small gaps between the bearing pads on the fuel and the pressure tube(32). The coolant flow rate is reduced in these crevices to such a degree that boiling can occur due to the heat flux from the fuel to the bearing pads. When this happens the saturation temperature of the solution increases. A very small superheating of less than one degree Celcius above the local saturation temperature is adequate to concentrate the dilute solution to the critical concentration within the crevice for accelerated corrosion to proceed.

In the case of thick oxides on the fuel rod surface, the local coolant chemistry may be modified by the high heat flux and the irradiation environment particularly under nucleate boiling conditions. When the pH level exceeds 11.3 in the presence of lithium hydroxide, there is an acceleration of the corrosion rate and an increase in the hydrogen pickup fraction. However from the extensive database of Zircaloy fuel clad corrosion behaviour under PWR conditions collected, Garzarolli et al(33) stated that since the increases in corrosion rates observed are not associated with an increase in the hydrogen pickup fractions, the role of lithium may not be significant.

Johnson(22) reported on the occurrences of relatively high deuterium contents in some Zircaloy-2 and -4 specimens exposed in an assembly at a fuel rod location in the Plutonium Recycle Test Reactor (PRTR), Hanford, Washington. Crevices were present between the specimens and the rod on which they were suspended. However, according to the author, the results (not given in his article) tend to suggest that a factor other than crevices contributed to the relatively high deuterium absorption of the Zircaloys.

Thus in the normal PWR environment, many factors can influence the corrosion rate and affect the hydrogen pickup in the zirconium alloys. The corrosion rate of Zircaloy is generally low with a high hydrogen pickup relative to its corrosion in BWR environment. The Zr-2.5 wt% Nb alloy remains consistent in having the lowest hydrogen pickup. Increased corrosion with low hydrogen pickup has been observed in high flux regions, around crevices and during coolant excursions into the less deoxygenated regimes. With the increase in oxygen content, the hydrogen content is reportedly reduced. The Zr-2.5 wt% Nb alloy has been reported to form nodules in the high flux regions in oxygenated conditions.

The longest exposure data examined in this work originate from the US and pertains to Zircaloy-2. No significant Soviet work on their operational experience in the PWRs have been obtained in this search. Most of the Soviet data contain generalized values on oxide thickness and hydrogen content of Zr-1 wt% Nb alloy after end of cycle observations.

The reports on long term exposure have indicated accelerated corrosion accompanied by increased hydrogen uptake can occur in Zircaloy-2 above a certain critical oxide thickness. A similar phenomena for Zr-2.5 wt% Nb alloy is questionable due to the more protective nature of its oxide and lower tendency for hydrogen pickup. However there currently is insufficient data to foresee the effects of thick films on the corrosion and hydriding behaviour of Zr-2.5 wt% Nb alloy in the PWR environment.

3. Dissimilar Metal Effects

The most extensive in-reactor zirconium hydride formation reported was from a hydriding phenomenon where Zircaloy-2 acted as the cathode of a galvanic couple formed with aluminum in the process water of the Hanford Production Reactor(34). The reactor is graphite moderated and light water cooled consisting of a core which is almost a cubical stack of graphite. The Zircaloy tubes are located in horizontal channels that penetrate the graphite stack front to rear and contain aluminum clad elements. The length of the tube contains several 20 cm long aluminum spacers for centering the fuel charge. The once-through reactor cooling water is Columbia River water with the pH adjusted slightly acidic with sulfuric acid (pH = 6.6) and contains 1 ppm sodium dichromate.

Examination of the Zircaloy-2 tubes after 2 years service revealed extensive zirconium hydride formation in the downstream portion of the tubes where the aluminum spacers were located. The hydrogen pickup and hydride case formation were attributed to cathodic charging of hydrogen into the Zircaloy. About 95% of the hydrogen was contained in the case which had concentrations of up to 2480 ppm. The base metal concentration was approximately 75 ppm with a suggested initial tube concentration of about 10 ppm.

The differences in composition of the aluminium alloys coupled to the Zircaloy-2 are thought to have a significant effect on the amount of hydrogen which can be cathodically introduced. The spacers were fabricated from one type of aluminium alloy, Type 6063 while the fuel elements were clad in Type 8001 alloy and were autoclaved. Examination of the longitudinal profile of the tube indicated that in general, the hydriding was limited to the downstream length of the tube where the aluminium spacers were located. The aluminium oxide film autoclaved on the element fuel cladding could possibly assist in reducing corrosion rates and the resulting corrosion (hydriding) currents.

Oxide films, formed by either anodizing aluminium or autoclaving zirconium, were used to investigate the effect of insulating one material from another. None of the pretreatments were completely effective in eliminating hydriding when the coupon was exposed in an aluminium holder. The autoclaving prevented uniform case hydriding, but local attack did occur at imperfections or breaks in the oxide film.

Other zirconium alloys tested, Zircaloy-4 and Zr-2.5 wt% Nb, appeared to be as susceptible or even more susceptible to hydrogen pickup under conditions conducive to cathodic charging.

The prospect that radiation may generate a potential between dissimilar metals or influence transport processes in the oxide have been studied in Zircaloy-2 and Zr-2.5 wt% Nb alloy by Johnson(22). In the ATR tests, Zircaloy and Zr-2.5 wt% Nb coupons with welded platinum inserts were exposed in the oxygenated and low-oxygen coolants(2). Weight gains were consistently higher on coupons having inserts, compared to irradiated controls. Thick oxides and gross hydriding were observed in the metal surrounding the welds but oxide thicknesses at locations away from the inserts did not appear to have been influenced by the short circuits. Exposures of unwelded inserts with these alloys in the ETR low-oxygen coolant showed no influence of the platinum on corrosion or hydriding for exposures of 60 days, 3 X $10^{20}n/cm^2$.

Controlled experiments have been performed on explosively bonded Zircaloy-2/Inconel 600 couples in the test reactor ETR G-7 loop at 270 - 280°C in pH 10 NH_4OH (< 0.05 ppm O_2)(22). The 146 day (1.5 X $10^{21}n/cm^2$) results indicated that intimate contact of these dissimilar metals caused accelerated attack at all locations where the two metals intersect in contact with the coolant. Gross hydriding was observed immediately under the Inconel, which was not dependent upon the accelerated corrosion since it was also observed in the 60-day specimens where accelerated corrosion had not occurred. Hydrogen absorption was accelerated under the Inconel compared to absorption through the zirconium oxide film which did not appear to have enhanced hydriding. Metallography showed a decreasing hydrogen gradient moving away from the Zircaloy/Inconel interface. it is suggested that since nickel and its alloys have a relatively high permeability for hydrogen, the Inconel acted as a "window" for hydrogen ingress. Intermetallic species were also observed in the Zircaloy/Inconel bonds and it is speculated by the author that these could serve as alternate sites of entry for hydrogen.

An experimental element fitted with alternate stainless steel (type not specified) and Zircaloy grids was irradiated in the SGHWR reactor to assess the relative importance of flow and galvanic coupling at grid positions on cladding corrosion(35). The general observation made was of the occurrence of much heavier oxidation on fuel pins opposite the stainless steel grids. No significant changes in hydrogen pickup was reported, in fact a low uptake is associated with the heavy corrosion near to the stainless steel. A possible hypothesis as postulated by Trowse et al(12) is that the stainless steel grid acts as a cathode, discharging hydrogen which otherwise would be released at the Zircaloy and thereby shifting the balance of the radiolytic reactions in the water to more oxidizing conditions near the reacting surfaces.

Similar galvanic effects was also observed by Tsykanov et al(10) in the surface oxidation of Zr-1 wt% Nb fuel cladding after exposures of up to 8 years in the VK-50 reactor. At regions below the stainless steel spacer grids, oxide film of up to approximately 500 µm were formed and further away in between the grids, the oxides were about 250 µm. No corresponding hydrogen values were reported for this case.

The galvanic coupling effects observed in the Hanford reactor between Zircaloy and aluminum alloys is a unique case of a totally different water chemistry. Insulating one material from another by anodizing or autoclaving, was found to be only partly effective in eliminating the hydriding. In the above environment Zr-2.5 wt% Nb was also found to be susceptible to hydrogen pickup.

In the PWR or BWR waters, galvanic and/or "window" effects between zirconium alloys and platinum, Inconel or stainless steel have been observed. Except for some Canadian work, no systematic work has been reported on the galvanic effects of dissimilar metals on Zr-2.5 wt% Nb alloy. Accelerated corrosion has been observed in Zr-1 wt% Nb alloys influenced by galvanic action and possibly some other effects. Under such similar conditions Zr-2.5 wt% Nb alloys may experience more severe corrosion with less hydrogen pickup.

4. Gaseous Environment

In the SGHWR and PHWR reactors, pressure tubes are used to convey the coolant through the reactor core at approximately 300°C. The pressure tube is insulated from the cooler moderator by a gas-filled annulus of carbon dioxide or nitrogen. The outside of the pressure tube is in contact with this gas which unavoidably contains some moisture and air as impurities. Consequently oxidation and hydrogen pickup can also occur at the outer surface of the pressure tube.

Studies of the effects of radiation on the oxidation of zirconium alloys in gaseous environment have been relatively few in number by comparison with investigations of primary water corrosion where higher oxidation rates and effects of radiation are encountered.

At low temperatures (up to 400°C), zirconium alloys have adequate resistance against carbon dioxide. Parfenov et al(11) in a review paper, reported that in CO_2 at 300°C and 8 atm. (0.8 MPa), Zircaloy-2 possesses high corrosion resistance (weight gains of 4 and 5.5 mg/dm^2 after 60 and 145 days respectively). The resistance of Zr-2.5 wt% Nb under the same conditions is reported to be only half that of Zircaloy-2 (10.5 and 12.5 mg/dm^2 respectively). No further details were given. In water at 325°C, the resistance of Zr-2.5 wt% Nb is stated to be adequate for use in power reactors. Addition of copper to this alloy somewhat reduces the corrosion of the alloy in water and steam but greatly increases its corrosion resistance in carbon dioxide and air.

Asher et al(36) investigated the corrosion behaviour of zirconium alloys exposed to moist carbon dioxide-air mixture at 300°C ($\sim 4 \times 10^{13}$ n/cm^2, > 1 Mev) in the PLUTO reactor at Harewell. The general implication of the work seems to be that the corrosion of Zircaloy-2 and Zr-2.5 wt% Nb in moist carbon dioxide-air mixture at 300°C is caused mainly by the moisture, with possibly a small contribution from the air. The carbon dioxide, although present in large excess appears to be relatively inert.

The corrosion of Zircaloy-2 is significantly enhanced by reactor radiation during exposures of up to approximately 800 days, but the hydrogen pickup is reduced from ~ 10% to ~ 3%. Figure 14 shows the effect radiation has on the corrosion rate of Zircaloy-2 and the various heat-treated Zr-2.5 wt% Nb alloys with behaviour ranging from a slight depression to a significant enhancement depending on the metallurgical condition of the alloy. The three different metallurgical conditions studied gave very similar in-reactor corrosion rates despite considerable differences out-of-reactor. The percent hydrogen pickup appeared not to be affected by the irradiation.

Improving the purity of the gas mixture by reducing the concentration of air from 1.5 vol% to 0.08 vol% had little effect on the corrosion rate of Zircaloy-2 or Zr-2.5 wt% Nb out-of-reactor but appeared to cause an increase in the hydrogen pickup for Zircaloy-2, Figure 15. The increase in percentage hydrogen pickup is perhaps by as much as twofold, while with cold-worked Zr-2.5 wt% Nb alloy, the effect is considered insignificant.

In predicting the corrosion behaviour of a typical reactor pressure tube made of Zircaloy-2, Asher et al(36) estimated an oxide film thickness of ~ 77 µm (after approximately 27 years) and the resulting loss in strength of the pressure tube is considered not to be significant. The hydrogen pickup would correspond to ~ 28 ppm which would not be detrimental since the authors considered that generally several hundred parts per million of hydrogen would be required to cause serious deterioration of the mechanical properties.

None of the three conditions of Zr-2.5 wt% Nb alloy studied (annealed; quenched + 3d temper; quench + 7d temper) showed any effect of radiation on hydrogen pickup rate. Using the conservative pickup rate for Zircaloy-2 (i.e. 0.12 mg/dm^2.day) and considering a thinner thickness to be used, the longtime hydrogen content would reach approximately 40 ppm which is again considered to have insignificant effects on the mechanical properties of the alloy for usage in the SGHWR reactor.

Asher et al(36) also pointed out the differences between the conditions in a typical pressure tube reactor and these in-reactor experiments. The lower gas flow rate in the tests was considered not to have a great effect on corrosion of these alloys. Reactor pressure tubes are usually pickled and prefilmed to about 20 mg/dm^2 before usage whereas the test specimens were merely degreased. However the authors believe that the prefilming treatment would unlikely have a long term effect on the in-reactor corrosion.

Bradhurst and Heuer(37) report on similar tests carried out (by Hurst and Tyzack) in the DMTR (no terminology given) at temperatures 310 - 315°C for up to 133 days. Increases in the corrosion rate of between 2 and 6 times were found for Zircaloy-2, whereas little or no changes were found for the Zr-2.5 wt% Nb alloy.

The activation energies obtained for the out-of-reactor oxidation of zirconium alloys in moist CO_2 at 300 - 595°C are of the same order as the values for the diffusion of oxygen in zirconium oxide supporting a mechanism in which the rate-determining step is the diffusion of oxygen through the protective oxide layer(37). No significant effects of surface preparation were observed since mechanical polishing or etching of the surfaces prior to oxidation showed no apparent changes in the oxidation of the alloys in the moist CO_2 environment.

Early hydriding experiments carried out in gaseous hydrogen at 400°C showed that it was possible to hydride Zircaloy-2 samples to hydrogen contents well above the solubility limit at 400°C (about 250 ppm)(38). Many variables were studied to determine the factors affecting the hydriding process for producing ideal specimens for assessing the properties of hydrided zirconium alloys.

Normally, the rate of absorption of hydrogen into the zirconium alloy is restricted by a surface oxide film and the rate at which the hydrogen can permeate this film is a function of the structure and constitution of the oxide layer. Hydrogen transport through the zirconium oxide film is via anion vacancies and line and lattice defects such as grain boundaries and dislocations(38). Cracks which develop on an oxide film may also provide an easy diffusion path. Many factors could affect the hydrogen transport rate through the film by modifying the extent of the above defects. Anion defect concentration will be affected by the temperature of its formation, the presence of impurity atom in the oxide and the oxidizing species in the gas phase.

Work has been performed by Winton and Farrow(38) to attempt to control the film permeability by modifying the surface condition and the nature of the surface film. Grit blasting or pickling did not appear to have a consistent effect on the hydrogen permeation through the oxide film, neither did preformed oxide films produced by controlled oxidizing treatments. The rate of ingress of hydrogen was found to largely control the incidence of hydride layering in Zircaloy. Only at ingress rates below 10 ppm/h could high hydrogen contents above the solubility limit be obtained with any certainty. The concentration gradients, and therfore the degree of layering can be modified by such factors as impurities in the metal surface and surface inhomogenities of texture and cold work. The impurities at the metal surface give indications of increasing the tendency to layering but the effects of texture and cold work have not been included.

Winton and Farrow demonstrated that it is possible to promote high hydrogen uptake with little layering by destroying the oxide skin in the hydriding furnace via a chemical reaction with CCl_4 and then effectively controlling the rate of absorption by controlling the rate of entry of hydrogen into the furnace.

From mechanistic studies, Shannon(39) also showed that the primary factor controlling the hydrogen absorption of zirconium alloys in gaseous atmospheres containing hydrogen is the rate at which oxidant (H_2O) is transferred to the metal surface from the environment. It was demonstrated that at sufficiently low oxidant concentrations in the presence of an inert carrier gas, the oxidation rate can be reduced, due to local depletion of the oxidant. Once the oxidation rate becomes limited, severe hydriding can occur at low hydrogen pressure (7 mm Hg), and relatively low temperatures (150°C). This can occur within a few days as the pre-existing autoclave films offer only transitory protection. The Zircaloy-2 samples (freshly etched and pre-autoclaved) were exposed to a purified helium-1% H_2 mixture which had all oxygen and water-vapour removed. Different temperature runs were made at 100 - 400°C. The specimens were considered to have "failed" when the first visible spalling due to hydriding was observed.

By noticing the large decrease in electrical resistance (10^6 ohms) of ZrO_2 corrosion films when the atmosphere was shifted from oxidizing to non-oxidizing, Shannon(39) suggested that the acceleration of gas phase hydriding may be due to a higher hydrogen diffusion rate created possibly by an increase in the concentration of oxygen anion vacancies in the film.

The hydrogen pickup of Zr-2.5 wt% Nb in various conditions is found not to be significantly affected by moisture in CO_2 environment. Though Asher's predictions of lifetime oxide thickness and hydrogen content may be conservative, these values should be of concern in thick films and delayed hydride cracking phenomena when other sources of oxidation and hydriding are considered. In the case of gaseous hydriding, the protective nature of the oxide film together with the presence of oxidants appears to control the ingress rate of hydrogen into the alloy (Zircaloy-2). Further studies are required to thoroughly evaluate and study the behaviour of Zr-2.5 wt% Nb in similar situations.

D. SIGNIFICANCE OF ALLOYING ELEMENTS ON CORROSION

The principal question covered in this section is: Do micro-alloying differences between zirconium alloys affect their respective corrosion rates? The major effect of alloying elements in the corrosion of zirconium alloys is on the properties of the oxides formed. These properties control the kinetics of the corrosion process and influences the absorption of hydrogen into the alloy.

The majority of the work reported deals primarily with the effects of major alloying elements on the corrosion and hydriding behaviour of the zirconium alloys. Little work has been done to determine the influence of lot to lot variability on the corrosion behaviour of the alloys. This is probably because of the many uncertainties involved and the long term duration of the tests before any significant effects can be distinguished. Besides some short-term tests on the influence of impurities usually beyond the specification levels, tests on the influence of heat-treatment on corrosion behaviour have also been reported.

1. Alloying Elements

The choice of alloying elements for the development of improved zirconium-base alloys has primarily been based on mechanical properties and corrosion resistance considerations. These improvements are likely obtained by alloying with elements from Groups VA, VIA and possibly Group VIIIA of the Periodic Table. From Wagner-Hauffe's principles, it is indicated that for anion deficient oxide forming metals (eg. Zr), the introduction of alloying metal ions which have a higher valency than the base metal might be beneficial from a corrosion viewpoint, providing the alloying oxide is soluble in the base metal oxide. In accordance to these principles, niobium, which has a valency of 5 when alloyed with zirconium, seems to promote low corrosion and hydrogen absorption behaviour in water up to 300°C and reasonable oxidation resistance up to 500°C in high pressure steam. The addition of tin (valency 4) appears to provide a mildly beneficial influence on corrosion in aqueous media up to approximately 350°C, but in 450°C steam and at higher temperatures, particularly at high pressures, its presence becomes significantly detrimental. Tin is an alloying element which is supposed to be effective in counteracting the adverse effects of nitrogen in aqueous out-of-reactor corrosion at 300°C.

Among the β-retaining elements, Nb and Ta form no intermetallic phases in binary alloy systems with zirconium while V, Cr, Fe, Co, Ni, Cu form phases of the eutectoid type including intermetallics. Generally coarse particles, agglomerates and selective grain-boundary precipitates tend to decrease the corrosion resistance. Better resistance to corrosion is obtained only when they are present in small amounts and when there is a fine uniform distribution of the second phase.

Working with very pure zirconium (electron beam refined crystal bar) and zirconium-iron alloys, Blanchet et al(40) found that the corrosion rate decreased rapidly with increasing iron content as shown in Figure 16 for alloys in either the cold-rolled or annealed conditions. Iron is added to the widely used alloys, Zircaloy-2, Zircaloy-4 and Ozhennite 0.5 to stabilize their corrosion resistance in water at high temperatures. Table III shows a list of the various zirconium alloys with their major alloying elements. Chromium is also one of the alloying elements of the Zircaloys and is added for a similar reason as iron. The published data on the influence of chromium on binary alloys are somewhat contradictory. The influence on the corrosion resistance of zirconium alloys has been reported as positive and negative. In tests carried out by Klepfer et al(41) on binary zirconium-chromium alloys containing 0 to 2.6 wt% Cr exposed to steam at 500°C for 1500 hours, it was found that on increasing the chromium content from 0 to 1.6 wt% the corrosion rate decreased from 10 to 6.5 mg/dm^2.day but on further increase in Cr content, the corrosion rate rose to 8 mg/dm^2.day. The beneficial behaviour of iron and chromium has been attributed by Berry et al(42) to the cathodic nature of the intermetallic compound particles existing in the zirconium matrix. The resulting potential difference is said to be sufficient to anodically polarize the zirconium thus improving the corrosion resistance. The compounds readily depolarize hydrogen and decrease the possibility of migration into the oxide film.

Nickel can confer oxidation resistance at high temperatures particularly in superheated steam, but is generally associated with high corrosion hydrogen absorption. The zirconium-nickel intermetallics supposedly act in the opposite direction to iron or chromium and enhance the ability of hydrogen to enter the film and evenutally end up in the metal substrate(42). It has been shown that nickel enriched Zircaloy-2 absorbs more hydrogen than that produced by the corrosion process when molecular hydrogen was present in the water or steam(43). Figure 17 shows the hydrogen pickup of the various alloying elements as a function of the alloy content. The most detrimental alloying element is nickel which shows enhanced hydrogen absorption. Tin is neutral, whereas iron and chromium at low levels reduced the pickup. Antimony is the most effective alloying element in reducing hydrogen pickup, but when added to Zircaloy-2 had little effect. Similarly additions of bismuth, arsenic and tellurium are neutral to hydrogen uptake when added to Zircaloy-2.

Yeniscavich et al(43) found that nickel content is an important variable in determining the hydrogen absorptivity of Zircaloy-2. For example, increasing the nickel content of normal Zircaloy-2 to 0.75 wt% resulted in an order of magnitude increase in hydrogen absorption during autoclave corrosion and two orders of magnitude increase during simultaneous corrosion and reactor irradiation. This increased hydrogen absorptivity appears to be a unique effect of nickel, because Zircaloy-2 specimens with increased iron and copper contents were also exposed to simultaneous corrosion and reactor irradiation and these elements were found to have no significant effect on hydrogen absorptivity. The authors theorized that the addition of nickel to Zircaloy-2 enhances its hydrogen absorptivity by catalyzing reactions with hydrogen which enhances the solution rate or mobility of hydrogen in the ZrO_2 film.

Kass(44) reported that nickel-free Zircaloy-2 and -4 are superior to Zircaloy-2 in water ≤ 360°C, because of their lower hydrogen pickup rates; however, above 400°C, Zircaloy-2 has better oxidation resistance.

Kiselev et al(45) also noted that zirconium-nickel alloys have a high affinity for hydrogen, even when the nickel content is low (up to 0.5 wt % Ni). The authors stated that the corrosion rate and therefore the hydrogen production rate of these alloys are low compared to those of zirconium-niobium alloys, but in spite of this their analyses indicated that the mass of hydrogen picked up by the zirconium-nickel alloys, for still unexplained reasons (according to the authors) exceeded that which was formed by corrosion.

In the various parameter studies on the corrosion of zirconium alloys in-reactor, Johnson(2) observed relatively low corrosion and hydriding rates on the Zr-2.5 wt% Nb alloy in both the ATR and ETR tests. The Zr-2.5 wt% Nb alloy in the annealed, cold worked conditions oxidized at rates similar to those of the Zircaloys in oxygenated coolants. Zircaloy-2 oxidized at rates similar to Zircaloy-4 in both ATR environments (0.6 ppm O_2 and < 0.05 ppm O_2). The hydriding resistance was somewhat better for Zircaloy-4 than for Zircaloy-2 agreeing with ETR results(24), however, both alloys had extremely low percentage hydrogen pickups at high weight gains. The difference in pickup for Zircaloy-2 and -4 is most pronounced in hydrogenated waters and this effect is shown schematically in Figure 18. Zirconium was found to have the poorest corrosion resistance in either environments.

The alloying of zirconium with niobium improves the strength characteristics of the alloys from ambient to high temperatures, and the corrosion resistance in water and superheated steam. Increasing the niobium content from 1 to 2.5 wt % decreases the corrosion resistance in pressurized water and steam(45) at temperatures up to 450°C, Figures 19 and 20. The tendency of zirconium alloys to pickup hydrogen is reduced by raising the niobium content. Table IV shows the hydrogen pickup by Zr-Nb alloys in pressurized water while the difference in pickup between Zr-1 wt% Nb and Zr-2.5 wt% Nb in a hydrogen environment is shown in Figure 21.

Kiselev et al(45) reported that alloys with niobium in the range 0.5 - 1.25 wt% Nb retains good corrosion resistance at temperatures up to 450°C. The authors considered Zr-1 wt% Nb to be the best alloy from the aspects of manufacturing, corrosion and mechanical properties. A comparison of the corrosion kinetics between Zr-1 wt% Nb and Zircaloy-2 showed that the long term (22000 hours) behaviour of the former alloy still follow the parabolic rate law whilst Zircaloy-2 shows a parabolic rate up to 2700 hours before accelerating at a linear rate when exposed to water at 360°C.

Ambartsumyam et al(46) also confirmed that unlike Zircaloy, Zr-1 wt% Nb and Zr-2.5 wt% Nb alloys do not show breaks in the oxidation kinetics during corrosion tests in water or steam/water system for times up to 2000 hours. However, as mentioned in an earlier section, long term tests in the VK reactor have shown that the Zr-1 wt% Nb cladding undergoes an accelerated corrosion regime after long term exposure.

Zaimovskii(8) in his review on the state of the work on Zr-Nb alloys developed and used in the USSR quoted that "it is the Canadian scientists that occupy the first place in these investigations" when referring to the extensive studies made on Zr-2.5 wt% Nb alloy.

The Zr-2.5 wt% Nb alloy has a corrosion mechanism which is similar to that of Zr-1 wt% Nb, but with a higher weight gain rate. In water at 300°C and 350°C, Zr-2.5 wt% Nb obeys the parabolic rate law from 500 to 14000 hours(45), Figure 26.

2. Impurities

The detrimental effects of certain impurities on corrosion are either to decrease the time to transition or to increase the post-transition corrosion rate constant by altering the oxide characteristics. A detailed analysis on the tolerance limits of nitrogen, aluminum and other impurities in Zircaloy-2 has been carried out(47) on batches which had impurities both within the specification limits and in some where the impurities were slightly higher. Based on these and other reported results, Gadiyar(47) specifies that Zircaloy-2 can tolerate the following impurity limits without any significant acceleration in the corrosion: (a) Al 140 ppm max., (b) N_2 100 ppm max., and (c) Mn 290 ppm max. No influence of oxygen contents in Zircaloys of up to 3000 ppm was noticed for specimens tested in water and steam at different temperatures(48).

One of the impurities having a significant influence on the corrosion behaviour of zirconium is nitrogen. In zirconium containing 70 ppm nitrogen tested in water at 370°C, the corrosion accelerated after 300 hours and the alloy was "completely destroyed" (weight gain 50 mg/dm^2) after 500 hours. Iodide zirconium containing 30 ppm nitrogen showed signs of severe corrosion (40% of specimen) after 3000 hours(46).

Ambartsumyan et al(46) has however pointed out that the harmful influence of one impurity can be countered by the effects of other impurities. The authors cited cases where certain heats of zirconium containing 50 ppm nitrogen had poorer corrosion resistance than other heats containing 100 ppm nitrogen and which had iron levels as high as 1500 ppm.

Kiselev et al(45) investigated the corrosion behaviour of various heats of Zr-1 wt% Nb and Zr-2.5 wt% Nb alloys in high temperature water and steam between 300 - 450°C for 14000 - 20000 hours. The following maximum impurity levels are recommended for effective corrosion resistance: nitrogen as 60 ppm, aluminum as 170 ppm and titanium as 160 ppm. However further experimentation with a specific Zr-1 wt% Nb heat (N_2 = 50 ppm, Al = 150 ppm, Ti = 50 ppm, Cu = 50 ppm, Si = 80 ppm, O_2 = 400 ppm) showed that a nitrogen content up to 130 ppm (with 150 ppm aluminum) did not result in excessive corrosion up to 4000 hours. Aluminum content can be increased to 220 ppm (with 50 ppm nitrogen) with no detrimental effects. Similarly titanium can be extended to the range of 160 - 200 ppm (in combination with 150 ppm aluminum).

Beyer et al(49) examined the corrosion behaviour of different melts of Zr-1 wt% Nb and Zr-2.5 wt% Nb in high temperature water and steam at 350°C and 400°C respectively. From the analysis of the same five different elements in each melt, Nb, O_2, N_2, H_2 and C (see Table V), it was not possible for the authors to obtain any decisive indications as to the influences of impurities on corrosion. The impurity levels of the elements investigated, except for carbon, were well within the range of specifications, Table III. Further investigation into the effects of other impurity elements showed that excess aluminum can have a significant effect on corrosion. Significant acceleration in weight gain occurs at levels $\geqslant$ 200 ppm Al for the Zr-2.5 wt% Nb alloy. However by increasing the quenching rate after annealing in the β-region, the effect of the aluminum content in Zr-2.5 wt% Nb is finally completely suppressed.

Parfenov et al(11) also consider nitrogen to be one of the most detrimental impurities in zirconium. The authors cited cases of specimens having nitrogen contents of 30 - 140 ppm which were found to have corrosion rates of 8.7 - 194 mg/dm^2 after testing at 315°C for 260 hours, Figure 22. There seems to be larger increments in weight gains for zirconium above about 70 ppm nitrogen content.

Huttig(50) cited investigations by other workers on the influences of nitrogen on zirconium and its alloys. Samples with more than 50 ppm nitrogen took about 12 days to reach the transition to white oxide formation when tested in high temperature water at 315°C. A Zr-Nb alloy with 1.45 wt% Nb and 170 ppm nitrogen failed completely in the static corrosion test and in a simulated BWR test at 288°C while an alloy with

1.87 wt% Nb and 50 ppm nitrogen had good corrosion behaviour. Huttig stated that the Soviet specifications for the Zr-1 wt% Nb alloy specify a nitrogen content of < 50 ppm.

Figure 23 shows the results of Huttig's work(50) on nitrogen in Zr-1 wt% Nb tested in 350°C water. After 2-4 days exposure the weight increases appear to be independent of nitrogen content. However for tests greater than 8 days, white oxide formation and spalling were observed on samples containing more than 133 ppm nitrogen. The white oxides appeared to grow preferentially on some grains while adjacent regions had firmly adhering black oxides. The author attributed this phenomenon to the anisotropy of growth of the oxide layer in these coarse-grained specimens. The results indicated that with increasing test time, the transition from black to white oxide formation is displaced towards lower nitrogen content. A similar trend was observed for nitrogen in Zircaloy-2, Figure 24. These observations indicate that in setting the specifications for the limiting contents of the harmful impurities, the particular material and expected service conditions (eg. temperature and time) should be considered.

Figure 21 shows the results of samples from two heats of iodide zirconium with different nitrogen contents, 150 ppm and 20 ppm, tested in gaseous hydrogen(46). The specimen with the higher nitrogen content showed a greater affinity for hydrogen.

The influence of the impurity silicon on the corrosion of iodide zirconium was studied by Ambartsumyan et al(46) in water at 370°C. Silicon levels from 0.10 wt% to 0.15 wt% is said to have a "favourable effect" on the corrosion resistance of zirconium while an increase in silicon content above 0.25 wt% diminishes the corrosion resistance.

Another deleterious impurity which can also accelerate the corrosion of zirconium in water and in steam is carbon. Tin can counteract this impurity to some extent. Carbon has a low solubility in zirconium and at levels around 0.1 wt% occurs in the metal as a carbide precipitate at around 300°C. In the form of carbides, carbon can lead to catastrophic corrosion. Beyer et al(49) quoted critical values from two different sources: 900 ppm for zirconium (German work) and 200 - 300 ppm for Zr-2.5 wt% Nb (Russian work). The Russian tests were performed with annealed Zr-2.5 wt% Nb (700°C) for test duration of 3000 hours. Lustman and Kerze(51) observed that oxide film breakdown occurred in zirconium over short times of exposure in water at 316°C if the carbon content exceeded about 600 ppm.

The influence of the impurity elements on the corrosion rate of zirconium alloys seems to involve a complex interaction of the other impurities and the major alloying elements. The common impurities which can be detrimental to corrosion resistance are nitrogen, aluminum, silicon and carbon. However when these impurities are kept within the specified permissible ranges, the general corrosion behaviour is usually acceptable. But the specifications that have been defined for a particular alloy may not be generally applicable to other alloys containing different major elements. This practice is currently acceptable since operating experience of the alloys has not proven otherwise or indicated the need to re-establish the impurity limits for the major zirconium alloys particularly Zr-Nb alloys.

3. Heat-Treatment

The corrosion rates of zirconium alloys are dependent on the type of heat-treatment and the fabrication history of the material. The microconstituents may to a certain degree influence the effects of heat-treatment and consequently the corrosion performance. However, the general types of structures and material properties expected from the various heat-treatment processes are usually predictable because of the major alloying components and the causes of any unusual corrosion behaviour are usually accredited to a combination of variables probably caused by manufacturing techniques and the presence of microconstituents.

The effects of fabrication and heat-treatment on the ex-reactor corrosion performance of Zr-2.5 wt% Nb have been the subject of many investigations. Among them are some significant Canadian studies which are internationally recognized. These studies are briefly referenced here since they have been acknowledged by foreign workers as being key papers.

The corrosion behaviour of Zr-Nb binary alloys was first reported by Ambartsumyan et al(46) who found rather poor corrosion resistance in 350°C water for samples that had been annealed in the range of 650 - 700°C. The alloys are very sensitive to oxygen in the coolant and to prior heat-treatment in ex-reactor experiments but show either minimum or negative acceleration due to the presence of neutron irradiation. Work by Klepfer(52) showed that suitable fabrication and heat-treatment could markedly improve the corrosion resistance. Material quenched from temperatures above the $\alpha + \beta$ phase (> 850°C) exhibited poor oxidation resistance in water, steam or CO_2. The quenched material retains all the niobium in solid solution and considerable improvement in oxidation resistance occurs with tempering at 500°C(53) and more particularly with 10-30% cold work between the quench and temper(54). Small precipitates were observed after ageing and the improved corrosion resistance was attributed to the presence of these particles. Figure 25 shows the beneficial effects of various degrees of cold working on samples quenched from 880°C prior to ageing at 500°C for 24 hours(55). All cold worked material resulted in lower weight gains than for Zircaloy-2 and the extent of the improvement increased with the severity of cold work.

Klepfer(56,57) studied the corrosion resistance of Zr-Nb binary alloys in a material development program for boiling water reactor service. Working with a series of alloys up to 5 wt% Nb subjected to different heat-treatments, it was observed that the α-treatment (8 hours anneal at 593°C + furnace cooled) alloys had the lowest weight gains while the β-treated specimens (β-Q: 2 hours at 927°C + quench in water; β-SC: 2 hours at 927°C + air cool) had higher corrosion rates at 360°C and 482°C. The β-SC specimens had the highest weight gains and also the largest hydrogen uptakes.

In metallographic studies, Klepfer observed apparently different "phases" in the photomicrographs which are believed to be zones of alpha zirconium formed in different ways: primary alpha rejected from beta zirconium in the range 845 - 605°C; alpha formed below 605°C by the decomposition of high columbium beta zirconium (formed on cooling or holding between 845 - 605°C); or alpha formed from supersaturated solid solution by the martensitic transformation. The author found that the change in corrosion due to heat-treatment did not agree quantitatively with the amount of "second phase" present and suggested the corrosion behaviour may correlate with the niobium content of the alpha matrix which seems to determine corrosion behaviour through its presence and uniformity in the corrosion film. The presence of precipitate is considered not of primary importance since the lower Nb content single phased alloys had good resistance at 360°C and 400°C. A fine distribution of the equilibrium beta niobium second phase is found in the most corrosion resistant specimens. This is a result of heat-treatment that promotes the proper matrix composition for good corrosion resistance.

Beyer et al(49) suggested that the optimum heat-treatments for good corrosion resistance in pressurized water for Zr-1 wt% Nb is an anneal at 700°C followed by slow cooling. The authors believe that the most effective and consistent method for the Zr-2.5 wt% Nb alloys is to subject the alloy to a quench from the β-region at the fastest rate possible. The authors attributed the inconsistent corrosion behaviour in the Zr-2.5 wt% Nb alloys to the possible influence of the impurity aluminum.

Parfenov et al(11) in an extensive Russian review on corrosion of zirconium alloys, quoted that investigation of the alloy Zr-2.5 wt% Nb has shown that after 30% cold working, the corrosion resistance in steam at 400°C (1680 hours) is better than after low or high temperature annealing (580°C or 800°C for 24 hours) or quenching in water from 1000°C. Referring to Cox's and Ells' work, they suggested that the high corrosion resistance found in cold worked Zr-Nb alloys is apparently due to the dominant influence of texture (preferred orientation of the grain structure). Regarding some European workers' opinion and observations that heat-treatment has little influence on the hydrogen pickup of zirconium alloys, the authors disagreed arguing that since the hydrogen pickup takes place through the oxide film, then the properties and conditions of formation of these oxides are greatly influenced by the structure of the metal, which in turn is dependent on the heat treatment.

Cold rolling and annealing of Zr-2.5 wt% Nb alloy at < 700°C also produces similar oxidation behaviour to the quenched, cold worked and aged alloys(35,55). Gadiyar(58) found that cold working up to 20% does not influence hydrogen pickup to any great extent, but excessive cold work (above 50%) does give rise to an increase. No reference to the sources of this information was given.

Tyurin et al(59) investigated the corrosion resistance of welded joints in Zr-2.5% Nb in a steam-water environment and suggested an effective means of increasing the corrosion resistance of the joints was to introduce surface plastic strain by roller burnishing in conjunction with subsequent annealing in the α + β range. The specimens were tubes of 88 mm OD and wall thickness of 4 mm which had been cold rolled 6-65% and annealed at 460°C for 5 hours. The specimens were edge grooved and butt welded by electron beam welding and subjected to a stream of steam-water mixture at 290°C. The corrosion resistance was by visual examinations on the basis of the colour and condition of the oxide film, the thickness of the oxide film and the change in specimen weight after testing. It was considered that a specimen coated with a dense shiny black oxide film has high resistance whereas one coated with a grey or white flaking film has low corrosion resistance. The results indicated that neither surface nor volumetric plastic strain without subsequent annealing improve the corrosion resistance of welded joints over those in as-welded condition, Table VI. Annealing of the specimens was carried out at 550°C for 5-10 hours. Cold working over 50% strain provided the most pronounced improvement in corrosion resistance and the burnishing operation was found to affect the structure to a depth of 300 - 350 µm which according to the authors is several times greater than the thickness of the protective oxide film (25 - 30 µm) that form on zirconium alloys after long-term service.

Kiselev et al(45) reported that the residual stresses can be reduced and good corrosion resistance restored in the welds and heat-affected regions of the Zr-2.5 wt% Nb alloys by a brief annealing at 700°C, since tests of these welds, carried out in water at 350°C for 6000 hours show, that black protective oxides are formed on the weld and heat-affected zones. However when Cheng et al(60) subjected the welds to only post-weld ageing at 500 - 565°C before exposure to the oxygenated water of the SGHWR (1014 days), they found that the weld zones were still susceptible to accelerated corrosion. Oxide spallation was observed at the heat-affected zones of the welded samples and the hydrogen content was found to be relatively low, around 22 ppm.

Johnson(2) exposed Zr-2.5 wt% Nb coupons in the quenched, cold worked, aged (Q,CW,A) and annealed (700°C), cold worked conditions in the ATR coolants. The former coupons were quenched from 870°C, cold worked 20% and aged at 500°C for 24 hours. The Q,CW,A structure had much better corrosion resistance in oxygenated coolant (63 mg/dm^3 against 189 mg/dm^3) but only slightly better resistance in deoxygenated coolant (17 mg/dm^3 against 25 mg/dm^3). Similar metallurgical conditions, investigated in earlier deoxygenated ETR loop tests showed similar corrosion response (28 and 52 mg/dm^3) after 174 days, instead of after a shorter duration of 62 days for the ATR tests(24). One of the prefilmed Q,CW,A specimens (13.4-14.6 mg/dm^3) obtained the highest hydrogen pickup (14%) among all the Zr-2.5 wt% Nb alloys (3-5% pickup) after exposure in the deoxygenated environment.

Amaev et al(61) conducted tests on heat-treated zirconium alloys in the steam and water cycle loops of the MR reactor for up to 145 days (O_2 = 12-17 ppm, $3.7X10^{20} n/cm^2$). The Zr-1 wt% Nb alloy showed up to twice the weight gain of the Zr-2.5 wt% Nb alloys in the annealed conditions (5 hours at 500 or 580°C). In the quenched and aged condition (Q,A: 800°C + 24 hours at 450°C) both Zr-2.5 wt% Nb and Zr-2.5 wt% Nb 0.5

wt% Cu showed similar weight gains of 53 mg/dm^2. Annealing Zr-2.5 wt% Nb at 580°C resulted in the highest weight gain (86 mg/dm^2) followed by annealing at 500°C, while the Q,A specimen had the lowest weight gain. The Q,A specimens had higher hydrogen contents than the annealed specimens (89 ppm and 60 ppm respectively for the Zr-2.5 wt% Nb alloys; 70 ppm and 47 ppm for the Zr-2.5 wt% Nb 0.5 wt% Cu alloys).

S. Kass(62) observed that the corrosion behaviour of Zr-2.5 wt% Nb-0.5% wt% Cu alloy is markedly dependent upon heat-treatment. The $\alpha + \beta$ treatment (824°C) followed by rapid cooling and a subsequent anneal at 538°C, produces excellent corrosion resistance in 316°C and 360°C water. The corrosion resistance has been shown to improve with more rapid cooling from the $\alpha + \beta$ region prior to the alpha annealing. The hydrogen absorption characteristics of the material, heat-treated for optimum corrosion resistance, have been shown to be very poor in 316°C water although, in 360°C water, the hydriding rate is less than that obtained by Zircaloy-4.

The most detrimental effect on the corrosion of Zircaloy arises from heat-treatment at about 1000°C followed by slow cooling. The formation of stringers of intermetallic particles resulting from the slow quench is associated with local areas of high corrosion at which white oxide spots can form. Quenching from the same temperature gives a more even distribution of small particles and provides enhanced resistance to corrosion.

Sumerling et al(35) compared the oxidation behaviour of Zircaloy in the stress-relieved (4 hour at 505°C) and fully recrystallized (1½ hours at 575°C) conditions in the SGHWR environment. The results from elements with recrystallized cladding show that the oxidation resistance can be marginally improved by this treatment leading to finer and generally smaller coverage of nodular oxides.

Alpha anneals of up to 790°C did not consistently suppress nodular corrosion in autoclave tests(63). However quenching after alpha + beta (840°C) and beta (1010 and 1040°C) anneals proved effective in suppressing nodular attack in the Zircaloys. Johnson and Horton(63) suggested that local variations in dissolved alloy content or second phase particle distribution are two potential explanations for promoting the localized corrosion penetrations.

The most significant influence of alloying elements on the corrosion behaviour of zirconium alloys is probably by the formation of the second phase particles which can be effectively controlled by the proper heat-treatment. Quenching and annealing to redistribute (homogenize) these particles appear to be the most popular and effective means of reducing corrosion. However by this method of optimizing corrosion behaviour, there appears to be a higher tendency for hydrogen pickup by the Zr-Nb alloys. The Q,CW,A treatments provides the Zr-2.5 wt% Nb alloys with best corrosion resistance while the annealed and cold worked condition showed almost comparable resistance in deoxygenated water. No reports of any significant influences of the microconstituents on altering the properties of the desired structures attainable by heat treating has been observed in the literature surveyed.

4. Oxide Formation In Aqueous Environment

The influence of the alloying and impurity elements as well as environmental parameters on the aqueous corrosion of zirconium alloys have been subjected to a wide variety of experimental and theoretical investigations with still no agreement or a unified perception of the corrosion process. However it is generally agreed that the beginning of the corrosion attack proceeds with the formation of a strongly adherent black oxide layer on the surface of the alloy. Then eventually, the black oxide loses its protective character and faster oxidation occurs at a somewhat linear rate resulting in the formation of white oxides. The manner and type of oxide formations is characteristic of the material condition and the type of alloying and impurity elements present, which to a significant degree controls the local progression of the corrosion process.

Ambartsumyan et al(46) observed that for Zr-Nb alloys tested in a 350 - 450°C aqueous environment, the oxide film spalls and flakes without a change in the colour of the film. Low niobium alloys have a dark brown film, getting lighter with higher niobium content. The special feature which the authors noted about these alloys is the absence of powder-like corrosion products in places where the oxide film had peeled off. These regions appeared a dark-gray colour. In those regions where the oxide had spalled, a new 'protective' film is formed. In comparison with unalloyed zirconium, the start of cracking and spalling of the oxide does not indicate the onset of accelerated corrosion. After 6000 hours in 350°C water, no spalling and cracking were visible to the naked eye at film thickness up to 30 microns on Zr-2.5 wt% Nb. At 400°C, the film became 50 - 55 µm after 6000 hours; no film spalling was observed. Cracking and spalling of the oxide film was only observed in the 5 wt% niobium alloy after about 3000 hours at 350°C. Figures 26 and 27 show the oxidation of these alloys in water and superheated steam. For alloys which the authors(46) consider the "Zirkalloy" type (0.1 Nb, 0.5 Sn with 0.2 Fe and 0.3 Ni), the thicknesses of the oxides were 15 µm at 350°C and 30 µm at 400°C after 6000 hours. No spalling or cracking were observed on these oxides.

Optical and electron microscopic examination of corrosion films on Zircaloy-4 revealed alternate dense columnar-grained layers and narrow porous layers lying parallel to the metal surface(64). The corrosion process consists of repeated cycles of the growth of a new protective layer at the metal-oxide interface. The layer suddenly becomes non-protective at a critical thickness causing transition to occur at the initially rapid corrosion rate. The cracks generated in the oxide always lay within the lighter bands indicating that the material there is weaker than the material in the darker bands. These cracks were later found to have resulted during specimen preparation. Thickness measurements showed that although the beta-quenched specimen had lower corrosion rate, the maximum depth of corrosion was nearly equal to that of the alpha-annealed specimen. The density of the film on the former specimen was found to be lower due to the presence of a higher volume concentration of pores and microcracks in the porous zones between the dense layers.

The alternate nucleation and growth mechanism for the oxidation of zirconium alloys is supported by further evidence from the study of Sabol et al(65), who observed alternating layers of these oxides on the Zr-2.5 wt% Nb specimens oxidized in 360°C water. The grain size of the pre- and post-transition oxide films on Zircaloy-4 and Zr-2.5 wt% Nb alloys were observed to be large (10 nm and 100 - 500 nm respectively) at the metal interface decreasing in size to 5 nm at the oxide water interface. The bulk of the post-transition oxide was highly porous having pore sizes from 1 nm to 15 nm and because of the connected pore networks was considered to be of non-protective character. No significant distinctions were observed between the oxides of Zircaloy-4 and Zr-2.5 wt% Nb except that some of the thicker films formed on the latter alloy had lateral cracks and had a more coarse structure than at the actively growing interface.

Stehle et al(66) observed that the bulk of the oxides formed on irradiated Zircaloy fuel rods from several PWRs have a spherical, granular microstructure providing for interconnected porosity within the oxide. A thin inner layer was observed at the metal interface whose structure was difficult to resolve with the scanning electron microscope (SEM). However it was stated that the in-reactor corrosion enhancement was greater for oxides which had a more pronounced granular appearance in this inner layer. Analysis of the oxide showed no indications of significant enrichment of chemical impurities from the primary coolant water. According to the authors, the progress of the post-transition corrosion in the PWR environment is partly due to irradiation accelerated recrystallization of the oxide especially at the inner layer and partly due to changes in the corrosive medium present in the porous outer section of the oxide.

In contrast to the findings of Sabol et al, Shirvington(67) observed that the most important corrosion resistant property of Zr-2.5 wt% Nb alloy (Q,CW,A) was that its oxide did not become as water permeable as the oxides of the Zircaloys in reactor environments containing free oxygen. The specimens used by Sabol et al were sheet-type specimens also in the heat-treated condition but quenched from a higher temperature of 950°C instead of 850°C and with no cold work before ageing. The corrosion weight gains of the Zr-2.5 wt% Nb specimens examined ranged from 32 - 750 mg/dm^2 while for Zircaloy-4 specimens, the range was from 16 - 183 mg/dm^2. This may account for the lack of differences in the morphologies of the oxides on the two alloys examined. Shirvington showed that the precipitation of niobium reduced the electronic and more particularly, the ionic conductances of the oxides. It is not certain what effect the niobium in solid solution (1.1 wt% Nb) might have on suppressing the formation of a permeable oxide. The results on Zircaloy-2 indicated that accelerated oxide growth on the alloy was due to an increase in the ease of solid-state oxygen ion diffusion and the shortening of pathways for such diffusion when the fine porous oxide becomes filled with water(17). The electronic conduction which was thought to most likely occur through intermetallic precipitates and other inclusions, was relatively unaffected by radiation.

No relationship has been reported on the role of microconstituents or alloying elements in defining the type of oxide formation during the oxidation of zirconium alloys. The prime objective of the studies surveyed on oxide formation was to explain the general mechanism and kinetics of the oxidation process. The findings of these studies indicated that oxide spalling can also occur in Zr-Nb alloys particularly with the higher niobium contents and that spalling may not have the same disastrous consequences as for zirconium. Except for the work of Sabol et al which briefly compared the oxides of severely oxidized Zr-2.5 wt% Nb to Zircaloy-4, no other studies were obtained which could clearly distinguish the characteristics of these oxides. The general attributes which have been suggested for differentiation are porosity (water permeability) and conductances of the oxide layer. The influences of microconstituents on these two properties and their role in corrosion behaviour have not been well investigated.

E. INFLUENCES ON HYDROGEN PICKUP RATE

The principal question covered in this section is: To what extent does the rate of hydrogen pickup depend on the hydrogen concentration in the material? The rate of hydrogen pickup depends on many variables, most of which have been discussed previously. Generally foreign researchers were more concerned with understanding the oxidation aspect of the corrosion process and treat the hydriding aspects as a secondary effect of the corrosion process.

1. Hydrogen Concentration

No direct evidence was obtained from the literature surveyed for a relationship between the rate of hydrogen pickup and the hydrogen concentration in the zirconium alloys. However some authors have made unsubstantiated remarks on the influence of hydrides or hydrogen on pickup and/or corrosion rates.

Commenting on the role of hydrogen in zirconium corrosion, Lustman and Kerze(51) stated that a high initial hydrogen content seems to accelerate the pickup of additional hydrogen . The authors were referring to the work of Goldman and Thomas(68) who subjected zirconium foils containing 10 ppm and 700 ppm hydrogen to 316°C degassed water containing 2000 cc hydrogen/kg water for periods up to 14 days. The hydrogen pickup for the two alloys were 44 to 109% and 190 to 350% respectively. Rubright and Koch(69) stated that there is a possibility that the hydrogen absorption process of the Zircaloys is auto-catalytic, i.e. material of high hydrogen content absorbs more hydrogen than does low hydrogen content material. According to them, no evidence is available to substantiate the explanation.

Kass and Kirk(70) evaluated the corrosion and hydrogen pickup behaviour of variations of Zircaloy-2 (normal, nickel-free, iron replaced nickel-free) in water (316°C, 360°C) and steam (400°C) environments. From sparse and widely scatered data, the authors concluded that for Zircaloy-2 (our assumption - all the three variations) the amount of hydrogen absorbed increased with exposure times. The rate of pickup appeared to them to be highest in early testing periods and continued to drop gradually with further exposure to 112 days. The percentage of absorbed hydrogen tended to be an essentially constant value (not given or suggested) which was relatively independent of test temperature.

Using data from other sources to illustrate the kinetics of hydrogen pickup by Zircaloy, Figure 28, Parfenov et al(11) outlined two distinct periods of hydrogen pickup. Initially the active growth of the oxide film is accompanied by intensive pickup of hydrogen. Then as a protective oxide film is formed, the hydrogen pickup rate decreases and stabilizes. As corrosion proceeds beyond the transition, the sharp increase in oxidation rate is accompanied by an increase of the hydrogen pickup. At transition, the momentary hydrogen pickup rate as suggested by the authors may exceed 100%. As a consequence of the different phases of the oxidation process, the properties of the oxide film are considered by Parfenov et al to be the determining factor in the hydrogen pickup of zirconium and its alloys.

Lustman and Kerze(51) stated that even though it has not been clearly established that hydrogen lowers corrosion resistance, the hydrogen picked up by the metal underlying the oxide film may possibly have an effect on the corrosion reaction through the formation of hydrides whose precipitation at the metal-to-oxide interface would destroy the coherency between the metal and the oxide. This effect will result in more rapid corrosion locally or possibly by loosening of the oxide. Thus the authors suggested that the formation of hydride may be the cause of the transition from the initial slow corrosion rate to the subsequent rapid rate.

Crystal-bar zirconium, sponge zirconium and Zircaloy-2 containing up to 1800 ppm hydrogen were machined and pickled and then corrosion tested in 400°C steam(71). The corrosion resistance of these specimens was not appreciably affected by increasing the hydrogen content of the metal. Schwartz and Vaughn(71) further studied the corrosion behaviour of the surface through which hydrogen has diffused. Corrosion tests were made on Zircaloy-2 specimens after 0 - 2500 ppm hydrogen had been added and with the specimen surfaces not machined or pickled before testing. The results after 18 hours testing indicated that the weight gain during corrosion increases linearly with the amount of hydrogen added to the metal through the corroding surfaces. In general, the hydriding treatment or the presence of the solid hydride phase decreases the corrosion resistance of Zircaloy(72).

In studying the corrosion behaviour of Zircaloy-2 in lithium hydroxide solution as a possible method of hydriding Zircaloy pressure tubes, Murgatroyd and Winton(73) observed that these specimens were all layered to some degree after hydriding. It is thus possible that the corrosion kinetics were influenced by the precipitation of hydride particles at the corroding surface since layered specimens were stated to apparently undergo earlier transition but for some time subsequently corrode at a slower rate than unlayered specimens. It was concluded by the authors that, during the corrosion of Zircaloy-2 in LiOH solutions (5 - 72 g LiOH/liter) at 300°C, the hydrogen absorption is approximately 65% of the hydrogen generated by the corrosion reaction and this value is not influenced by the thickness of the oxide film or the concentration of the LiOH solution, Figure 29.

In contrast to the high hydrogen pickup of the Zircaloy-2, Figure 30 shows the hydrogen weight gain in relation to the oxide weight gain for the Zr-2.5 wt% Nb alloy in 100 g LiOH/liter solution at 300°C(74). The amount of hydrogen absorbed is relatively low and is between 0.2 - 0.8%. This reference is Canadian and is included for completeness and comparison between the behaviour of Zircaloy-2 and Zr-2.5 wt% Nb alloy. The work suggests that there is change in kinetics in the hydrogen pickup at very high oxygen weight gains. But the percent hydrogen pickup at this stage is extremely low.

In summary, hydrogen present in zirconium alloys tend to increase the corrosion rate of the alloy probably by affecting the metal-oxide interface. The cases reported were mainly alloys with high hydrogen contents where the hydride already exist as solid precipitates. The case cited by Parfenov(11) describes the various pickup rates as corrosion progresses and tends to indicate that hydrogen pickup is more related to the changes in corrosion behaviour and the nature of the oxide film.

2. Other Effects

Besides the indirect influences on hydrogen pickup rate mentioned above, other more significant influences that have been considered by foreign workers and mentioned in the other sections of this report are the local environment, the type of alloy, and the nature of the corrosion film produced during the course of oxidation and hydrogen ingress. However no direct relationships between the pickup rate and any one of these variables have been confirmed for in-reactor tests.

F. DELAYED HYDRIDE CRACKING

The principal question covered in this section is: Is delayed hydride cracking due to high stress levels, low temperature gradients or other factors? A phenomenon that has emerged as a problem with the in-reactor usage of zirconium alloys is that of strength degradation due to the presence of hydrogen. Hydrogen which is usually absorbed during fabrication as an impurity or during service as a result of corrosion, may cause component failures after prolonged periods at stresses that are well within the normal load limits. This time-delayed failure is generally brittle in nature and is not accompanied by any large degree of plasticity of the bulk material. The final fracture is induced by the formation and growth of incipient cracks via the diffusion of hydrogen in the metal lattice to the stress sensitive regions. This process is commonly known as delayed hydride cracking (DHC).

After years of extensive theoretical and experimental studies primarily by Canadian researchers, the causes and reasons for DHC in zirconium alloys are becoming more clearly identified and accepted. The DHC process involves the stress-directed diffusion of hydrogen to a crack tip, followed by hydride precipitation and fracture of brittle hydrides and the subsequent arrest of the crack in the tougher zirconium matrix ahead of the hydride precipitates. The mechanism repeats itself allowing crack propagation to proceed in a discontinuous fashion. The distribution and orientation of the hydrides in relation to the applied stress appear to be the major factor in the delayed hydride cracking of zirconium alloys.

1. Distribution and Orientation

Hydrides can precipitate as needles when present in very small amounts (as low as 15 ppm) and then appear as platelets of zirconium hydride with increasing precipitation. These hydride platelets are generally oriented along certain crystal planes at grain boundaries and along slip planes, thus tending to restrict the plastic flow of the matrix to a certain degree.

The deleterious effect of hydrides on mechanical behaviour depends not only on the volume of hydride present but also on its distribution and morphology, particularly the orientation of the platelets with respect to any residual or applied stresses. Many possible planes of precipitation can exist and can change within a given sample upon the application of stress. It has been suggested by Kearns and Woods(75) that cold work affects the initial hydride orientation and not the orientation in stressed samples. Hydride orientations were measured in annealed Zircaloy-4 samples cooled under no applied stress and the orientations were found to correlate with the crystallographic texture of the basal poles. The fraction of hydrides located in a given region increases as the volume fraction of the basal poles present increases. The results of the investigation also indicated that the susceptibility to a change in orientation under applied stress is a function of cold work and grain size. The highest susceptibility to stress reorientation occurred in the finest grain material and increases with the fraction of grains oriented with their basal poles parallel to the stress axis.

Marshall(76) made a quantitative study of the effect of fabrication on stress orientation of hydride platelets. The susceptibility to stress orientation of the hydrides appeared to be a characteristic of the type of reduction. For hot reduced tubes, the susceptibility to stress orientation was very high; essentially 100% of the hydrides were reoriented at moderate stress levels. In contrast, the susceptibility was lower and very similar for all cold reduced tubing. The amount of reduction in diameter or wall thickness during fabrication did not greatly influence the susceptibility. Stress reorientation was by far the easiest in the direction of the material in which the major fabrication strain had been compressive. Conversely, very little stress orientation was exhibited in material directions in which the major strain had been tensile. Thus the stress reorientation should be most prevalent in the circumferential and radial directions of reduced tubes, the longitudinal and radial directions in expanded tubing and in the thickness direction of rolled plate.

The observation by Marshall of the importance of compressive strain during fabrication as the dominant factor affecting hydride orientation led to the development of a parameter, the directional strain parameter (DεP), which permits a single correlation to be made of a wide variety of tubing fabrication processes with the subsequent hydride orientation(77). The author stated that two orienting forces interact to determine the preferred orientation of the hydride platelets. Firstly, a "natural" orientation plane for subsequently formed hydride platelets is induced in the Zircaloy during fabrication and secondly the natural orientation can be changed if a stress sytem acts on the material matrix during platelet formation. This second phenomenon called stress orientation (or reorientation) tends to induce hydride platelet formation perpendicular to applied tensile stresses and parallel to compressive stresses. Thus the hydride orientation produced in zirconium alloys during service is the result of service stresses acting on the natural orientation distribution created during fabrication.

Hardie and Shanahan(78) also stated that in unstressed materials, the orientation of the hydride precipitates are closely related to prior strain (fabrication history) whereas in stressed materials it is dependent upon the texture and stress. The authors studied the factors governing the realignment of hydride platelets in Zr-2.5 wt% Nb plate material and tubing specimens under stress. Stress reorientation readily occurs providing that the fabrication texture of the material results in a high concentration of basal poles in the direction of applied stress. The results showed that only hydrides taken into solution can become oriented, because the stress affects precipitation during cooling under stress, and the maximum degree of reorientation is therefore dependent upon temperature and hydrogen content. Thus the cooling of hydrided specimens of Zr-2.5 wt% Nb under a tensile stress can result in an increase in the proportion of hydride platelets oriented perpendicular to the direction of the applied stress. The degree of reorientation is found to increase with increasing cold work and solution temperature.

Ushakov and Abramov(79) studied the effects of irradiation on the reorientation of hydrides in Zr-2.5 wt% Nb alloy subjected to tensile stresses at temperatures between 250 - 350°C. Irradiation may have a strong influence on the main parameters of the hydride reorientation process by affecting the mobility of the atoms and precipitation of the secondary phases. Referring to the work of Hardie and Shanahan(78), Ushakov and Abramov indicated that irradiation reduces the effective solubility of hydrogen in zirconium and leads to a reduction in the maximum degree of reorientation since only those hydrides which dissolve at test temperature can reorient themselves.

Jie et al(80) examined the texture, stress and reorientation of hydrides in hydrostatically extruded Zr-2.5 wt% Nb alloy tubes having basal plane normals in the radial direction. These tubes were hydrostatically extruded at room temperature, then stress-relieved (400°C) before subsequent cold reduction of 10%. The specimens were hydrided to about 80 ppm with the hydrides oriented circumferentially. The stressed specimens were heated at 400°C for 24 hours followed by slow cooling to room temperature. When the tube with circumferentially distributed hydride is subjected to hoop tensile stress and thermally cycled, the hydrides will tend to rotate to the radial direction perpendicular to the tensile stress and this stress is denoted by the authors as the "threshold stress for induced reorientation of hydride". Table VII shows the results of these tests. The hydrostatically extruded tube with the radial basal pole texture has a much higher hydride reorientation threshold stress than the conventional hot extruded, cold-rolled tube having the basal plane normal in the circumferential direction.

It has also been shown by Warren and Beevers(81) that the nucleation process of zirconium hydrides is independent of the orientations of the hydrides to the tensile axis. However the subsequent crack propogation within the hydrides has a strong dependence on the hydride orientation with respect to the tensile axis and is probably by a normal stress criterion.

Obara et al(82) found that the effect of hydride on the mechanical properties is dependent on the orientation of the hydride platelets relative to the stress axis in uniaxial and biaxial stress tests. The hydrogen contents of the specimens ranged from 30 - 500 ppm. Tests were performed from room temperature up to 400°C. The burst strength of the tubes was reduced by 60 percent between room temperature and 300°C (no hydrogen values given). In the specimen containing radial hydrides (no other details given), the circumferential elongation for room temperature fracture dropped from 8% at 30 ppm H_2 level to 1% at 120 ppm H_2. In the tube with circumferentially aligned hydrides "embrittlement was not obtained until the 300 ppm H_2 level". In both cases, the authors noted that ductility recovered when test temperature was increased from room temperature to 300°C, Figure 31.

In summary, the texture of the zirconium alloy and the nature of the of stresses encountered are considered significant factors by the above mentioned authors in determining the initial and reoriented hydride distributions. Radial hydrides are considered to be the most detrimental orientation for hydride in tube applications such as fuel rods and pressure tubes. The main approach to minimize radial hydride formation (and possible cracking) has been to produce a suitable initial hydride orientation through proper texture development, which will then require a higher threshold stress to reorient the hydride during operation.

2. Temperature Effects

Since hydrogen tends to concentrate at stress raisers and low temperature regions of a material, it is more likely to find hydride precipitation if there is a stress concentration and a low temperature. Redistribution of hydrogen will also occur under the influence of concentration and thermal gradients. The thermal gradients cause thermal diffusion which drives the hydrogen towards the colder parts of the component. The precipitation of zirconium hydride at any point where the hydrogen concentration exceeds the terminal solubility (~ 20 ppm at 300°C) constitutes a hydrogen "sink".

It has been shown(83) that under the influence of a temperature gradient, hydrogen in Zircaloy-2 will tend to move to the colder regions until a steady-state distribution, determined by the so-called heat of transport is attained. Shewman(84) has qualitatively discussed thermal diffusion and arrived at an expression for the hydrogen current in the two phase region enabling him to calculate the time to steady state.

No foreign reports were obtained pertaining to the effects of temperature on delayed hydride cracking.

3. Stress Effects

The driving force for the diffusion flux of hydrogen in the material is provided by the local stress gradient which interacts both with the hydrogen atoms in solution and hydrogen atoms being dissolved and reprecipitated. There is a stress effect associated with the hydrogen in interstitital solid solution in the metal lattice and another effect associated with the hydrogen precipitated in the form of hydride. No foreign literature was located where studies of the above nature were made pertaining to the delayed hydride cracking in zirconium alloys. Stresses are considered in the studies only on the reorientation of hydrides which have been discussed in an earlier section.

G. OTHER RELATED STUDIES

The articles reviewed in this section are included to indicate the foreign work that has been performed pertaining to pressure tube cracking.

Cowan and Cowburn(85) performed burst tests on Zircaloy-2 pressure tubes containing various amounts of hydrogen and having pre-existing cracks of various lengths. The critical crack length for rapid, uncontrolled failure to occur was determined. The effect of hydrogen was to markedly reduce the critical crack length for a given stress and temperature, but this embrittling effect is reduced with increasing temperature, Figure 32 and 33.

An analysis of critical crack lengths, including the effects of radial hydrides and neutron irradiation on Zircaloy-2 pressure tubes was performed by Watkins et al(86) using pressurized tests. Specimens with radial hydrides were produced by modifying the tube fabrication route (cold sinking) followed by hydriding under stress in lithiated water. This treatment resulted in about 90 percent of the hydrides being radial. Although the effect of hydrides was quite marked at 20°C, there was little or no effect on the critical crack length at 300°C. These values ranged between 76 - 101 mm. No effect of irradiation on these values were observed up to at least 10^{21}n/cm^2. The authors concluded that failure by unstable crack propagation was not likely to occur under reactor operating conditions.

Pankaskie(87) subjected Zr-2.5 wt% Nb tubes to cyclic internal pressurization to cause axial crack growth and unstable fractures at room temperature. The fracture toughness of cold-worked (30 - 60% reduction in area) samples in either the hydrided (200 - 300 ppm H_2) or unhydrided conditions is greater than for the heat-treated (880°C quench, 15% reduction and 24 hours at 500°C) samples. For heat-treated tubing the fracture toughness was reduced about one-third after hydriding.

Rao(88) analysed the high cycle fatigue crack growth behaviour of Zircaloy-2 and Zr-2.5 wt% Nb sheet materials at room temperature on the basis of fracture mechanics. It was found that the crack growth rate could be represented by a power rate law of the type $da/dN = C\ (\Delta K)^n$ where da/dN is the rate of growth, ΔK the stress intensity range, C and n are constants. A value of 3 for n was found to hold for both materials. The total effect of hydrogen was to increase the crack growth rate by increasing C but not n. The rate was higher for hydrided Zr-2.5 wt% Nb alloy than for Zircaloy-2 at a given stress level.

Honda et al(89) determined the fracture toughness of heat-treated (Q, CW, A) Zr-2.5 wt% Nb pressure tube by conducting pressurized (burst) and bend tests on specimens obtained from tubular sections. Although the fracture toughness of the alloy decreased with increasing hydrogen content, they considered it would be little affected by hydrogen content at reactor operating temperatures. Figure 34 shows the results of burst test of 41 mm ID and 57 mm ID, 4.3 mm wall thickness Zr-2.5 wt% Nb tubes which had notches of 3.3 mm depth on the exterior of the tube(89). The test was conducted at room temperature and the hydrogen content of the tube was 10 ppm. The experimental values of fracture stress versus crack length are shown together with values obtained by calculations. Figure 35 shows the results of tubes containing 100 ppm hydrogen which were tested at 150°C. The crack depths were varied from 2 - 4 mm. While there is no significant difference in the critical crack length between the larger and smaller diameter tubes at room temperature, critical crack lengths were observed to vary with crack depth at 150°C (the only temperature tested). An increase in crack depth results in a decrease in the critical crack length. The relationship between fracture toughness and hydrogen content at room temperature is shown in Figure 36. The fracture toughness values decreased with increasing hydrogen content but were little affected at reactor operating temperature (300°C) as shown in Figure 37. Defining the term radial hydride content (RHC) as the total length of the hydrides in a vertical direction projected onto the tensile stress direction per unit area, the authors(89) establish a relationship between fracture toughness and RHC. Figure 38 shows the relationship between RHC and the hydrogen content and the fracture toughness of the material can be obtained from Figure 39 which shows the relationship between the RHC values and fracture toughness. The authors suggest the above method for estimating the quantitative value of the fracture toughness of a zirconium alloy.

Pressurized burst tests were performed by Tsunoda(90) at room temperature on autoclaved and control Zircaloy-2 cladding tubes containing simulated scratches which were subjected to hydrogen absorption by both gas flow and lithium hydroxide methods(90). The scratches were ≤ 1% of the wall thickness 0.87 mm and was considered not to directly affect the burst strength. The authors observed that for the same hydrogen level (no values given) there was little difference in burst strength of the two material conditions. For the control specimen, there was no difference between the scratched region and the parent metal, but for the autoclaved tubes, more hydrides were observed segregating near the scratch. The authors contend that this effect causes local brittleness particularly in decreasing the circumferential elongation of the tube. No data was presented by the authors except for a photomicrograph of a brittle failure through a scratch.

Tyurin et al(91) concluded that the corrosion resistance of Zr-2.5 wt% Nb channel tubes (63 mm diameter by 4 mm thick) in the flow of steam/water mixture is governed by the quality of the surface finish. The corrosion resistance of the internal surface of the tube after testing for 18000 hours was found to be appreciably lower than the external surface. Scratches, microcracks and microruptures were observed in the inner surface which could account for the increase in corrosion. Hydride blisters have often been associated with scratches and other defects which have not been completely eliminated by pickling(72).

The critical crack length studies indicate that the crack length is of concern only at low temperatures. At 300°C, the influence of hydrogen is markedly reduced even with substantial amounts of radial hydrides and unstable crack propogation is considered unlikely. However this latter effect was studied only on Zircaloy-2. The critical crack length was found to decrease with crack depth in the Zr-2.5 wt% Nb alloy. Surface finish was also established to have a significant influence on localized corrosion and hydriding which might eventually become initiation sites for crack propogation. To reiterate, hardly any literature that is non-Canadian has been published on the topic of delayed hydride cracking.

H. SUMMARY AND IMPLICATIONS

This report describes a fairly exhaustive survey of the world literature on corrosion, hydriding, cracking and blistering of zirconium alloys. This survey has been conducted via both computer search of a number of data banks and personal contacts (letters or visits). In this search, we have been impressed by the significant number of Canadian papers which have been referenced in the international literature. The Canadian research is generally regarded in high esteem. In the particular area of delayed hydride cracking, it was evident from the survey that the Canadian work represents the bulk of the world literature; as an aside, this may be because other nuclear programs have not been faced with delayed hydrogen cracking problems because of the design or construction of their systems. It is believed that further access to some of the data from Russian and other Eastern Bloc countries may be helpful since such countries published little 'hard' data in the open literature and their openly publicized research programs do not seem adequate to support their extensive nuclear program. Much of the data we have found on Zr-1 wt% Nb for instance seem to be from the same series of tests with the results presented in a slightly different form in a whole series of papers. Apart from CANDU vendors, the Russians are also major users of Zr-Nb alloys.

It is also interesting to note that we heard through one of the contacts at CNEA Argentina that the Argentinians are embarking on a major program of studying the corrosion/hydriding behaviour of zirconium alloys, principally Zr-2.5 wt% Nb. Furthermore, Mr. Z. Jie of the General Research Institute for Non-Ferrous Metals, Beijing, China, wrote to indicate that they had data on Zr-2.5 wt% Nb other than that on hydrostatically extruded tubes but could not release the data outside China.

In terms of answering the four questions posed in the original Request for Proposal we have found that, in certain areas, there is a paucity of data for conditions similar to those of CANDU-PHW reactors and further work seems required. This situation is not surprising given the fact that the CANDU system is a unique design to which data from other reactor systems may not be directly applicable.

In the following sections, we will discuss the four questions posed in the Original Request for Proposal.

a) Is Corrosion the main agent for the zirconium hydride acquisition mechanism?

The basic $Zr + 2H_2O\ (2D_2O) \rightarrow ZrO_2 + 2H_2\ (2D_2)$ corrosion reaction appears to be the main route for the acquisition of hydrogen and the formation of zirconium hydride. The degree of hydrogen pickup depends on evironmental and material variables such as coolant chemistry, alloy composition, metallurgical and surface conditions, proximity of other materials and the thickness of oxide acquired. As well as the general corrosion occurring along the length of the pressure tubing or fuel sheathing in contact with the coolant, we must also consider the effects of galvanic coupling (to endfitting in case of a CANDU pressure tube) and crevice corrosion (at various locations, eg. endfitting, bearing pads, etc.). These effects could lead to accelerated corrosion locally and perhaps (although not necessarily) give rise to faster rates of hydrogen acquisition. Probably the most spectacular example of galvanic coupling was of Zircaloy-2 and aluminum in the Hanford Production Reactor. In this case, Zircaloy-2 acted as the cathode of a galvanic couple and there was cathodic charging of the hydrogen into the Zircaloy with hydrogen contents up to 2480 ppm being produced in the Zircaloy. A comment was made in a report of the phenomena that other zirconium alloys tested, eg. Zircaloy-4 and Zr-2.5 wt% Nb, appeared to be as susceptible or even more susceptible to hydrogen pickup under conditions conducive to cathodic charging.

Although the galvanic effects can produce accelerated corrosion, it is not necessary to have accelerated hydrogen acquisition and in fact the opposite can occur. For example, coupling of stainless steel (type not specified) and Zircaloy in the SGHWR reactor led to heavy oxidation, but no significant change in the overall hydrogen pickup. In fact, a low hydrogen pickup was associated with the areas of heavy corrosion. The hypothesis here is that the stainless steel acts as a cathode discharging hydrogen which otherwise would have been released at the Zircaloy and thereby shifting the balance of the radiolytic reactions in the water to more oxidizing conditions near the reacting surfaces. Possible scenarios for galvanic coupling would include the situations where:

1) a zirconium alloy acts as a cathode, causing cathodic charging to take place and the rate of hydrogen ingress to be accelerated;

2) the coupled material acts as cathode causing accelerated corrosion rate due to galvanic coupling and the formation of thicker oxides (these thicker oxides can themselves slow down the rate of hydrogen ingress although this may not be the case).

Hydrogen (deuterium) can also be picked up from the gaseous phase since there is $H_2(D_2)$ in the coolant and can be in the gas anulus of some reactors. Pickup rates through this route are considered to be low since the pressure tubes would have a protective oxide film which would slow down the ingress of hydrogen. Coupling with a material of greater permeability to hydrogen (deuterium) could produce greater ingress of hydrogen and this has been recognized as a "window effect" which seems to account for the higher deuterium levels in the pressure tubes near the endfittings. This window could also act in another manner in that because of corrosion reaction at or near the 'window material', hydrogen (deuterium) is released and then could be concentrated in the zirconium alloy through the window effect.

There is generally a lack of knowledge (or at least published data in the open literature) on galvanic coupling and crevice corrosion effects and present research efforts seem inadequate.

b) Do micro-alloying differences between zirconium alloys affect their respective corrosion rates?

In order to answer this question fully, one needs to know what was meant by microalloying. We have chosen to be as broad as possible and include both 'regular' alloying additions (≳ 0.1% levels) and impurities (≲ 0.1% levels) which are those from processing and from the zirconium base material. Considerable data was found on the corrosion rates in-pile and out-of-pile for a number of zirconium alloys. Most of these reports, particularly the earlier work, did not contain information on the concurrent (with corrosion) hydrogen acquisition.

At CANDU operating temperatures (~ 300°C) the Nb-containing alloys generally corrode faster than the Zircaloys, out-of-pile. The corrosion rate generally increases with the amount of Nb in the alloy. However, since the corrosion rate of Zr-2.5 wt% Nb appears to be only little increased by irradiation and sometimes even inhibited by it, in-pile corrosion rates during short term exposures are somewhat similar for the Nb-containing alloys and the Zircaloys.

The distinct advantage of Zr-Nb alloys over the Zircaloys is that Nb-containing alloys normally pick up a very small fraction of the hydrogen released by the corrosion reaction. However, the addition of small quantities of metals such as Fe, Cr, Ni to zirconium alloys gives rise to higher hydrogen pickup rates. This is not surprising since these intermetallic compounds of zirconium, which have potential use as hydrogen storage materials, are known to absorb hydrogen to a hydrogen-to-metal ratio as high as 1.4.

The Zircaloys are known to be prone to nodular corrosion in reactor environments. This local enhanced corrosion, which can be associated with increased hydrogen acquisition, appears to be related to the presence and distribution of intermetallic precipitates (Ni, Fe, Cr containing). Generally Zr-Nb alloys are not considered susceptible to nodular corrosion since the intermetallic precipitates are not found to any significant quantity in these alloys. A note of caution should be added here however since there really has been no detailed systematic study of these intermetallic precipitates in Zr-2.5 wt% Nb pressure tubing and there is a distinct possibility that on irradiation the Fe that is present (~ 0.05%) in solution could precipitate out of solution. However, nodular corrosion has been reported by Russian and Czech workers for Zr-Nb alloys in high flux, oxygenated conditions. No plausible reasons for the nodular corrosion have been advanced. The Russians claim their Zr-1 wt% Nb to be a single phase, but work in other countries (including Finland where they tested Russian fuel cladding) would rather suggest that it contains α-Zr and β-Nb(Zr). If it is the presence of the β-phase that gives rise to nodular corrosion then Zr-2.5 wt% Nb should be more susceptible since it contains more β-phase than Zr-1 wt% Nb. As an aside, it should be noted that it is a general rule in corrosion behaviour that the more homogenous a material then the less likely it is to suffer localized corrosion. The presence of intermetallic precipitates or second phases should increase the probability of localized corrosion.

A more general point is worth noting in this connection. With respect to the microstructure and properties (including corrosion) of zirconium alloys, there seems to be a lack of knowledge and research on second phase particles; i.e., what exactly are the particles and how do they affect the microstructure and consequently the properties of the alloy. The second phase particles would include not only the Ni, Cr, Fe containing intermetallics such as those found in the Zircaloys, but also carbides, phosphides, and silicides which are present to some degree in all commercial zirconium alloys together with the second phases due to a significant degree of alloying, eg. β-Nb(Zr).

c) To what extent does the rate of hydrogen pickup depend on the hydrogen concentration in the material?

As with question b) there was some doubt as to the particular concern in mind when this question was posed. On reflection, it seems likely that there was concern as to whether there was a 'breakaway' phenomenon in hydrogen pickup similar to that noted for the oxidation and weight gain (oxide thickness) in corrosion.

In general, there can be an increase or decrease in the rate of hydrogen pickup at various stages in the hydriding reaction. Rather than being related to the hydrogen content of the material per se, the hydrogen pickup rate appears to be related to the changes in corrosion behaviour and the nature of the oxide film. Spalling of the oxide or a high level of porosity can lead to higher hydrogen pickup rates. There is evidence for the Zircaloys that the hydrogen pickup rate may undergo a 'breakaway' similar to that observed for the oxidation rate. No such 'breakaway' has been observed in Zr-Nb alloys in in-reactor tests, but test durations have been relatively short.

Of course the predictions and the accompanying confidence in the satisfactory long-term behaviour of the system would be misleading, particularly if other operational factors could lead to concentration of the H(D) at selected sections of the pressure tube. Factors leading to concentration of H(D) would include stress concentrations and temperature gradients. Working against these factors there could be a driving force which causes diffusion down a concentration gradient and consequently a removal of, or at least reduction in, the concentration gradient.

d) Is delayed hydride cracking due to high stress levels, low temperature gradients and/or other factors?

For delayed hydride cracking (DHC) to occur, one requires both the presence of precipitated solid hydride and a stress of sufficient magnitude and direction to crack the hydride. Since hydrogen concentrates at stress raisers and low temperature regions in the component, one is more likely to have solid hydride if there is a stress concentration and a low temperature.

Since the hydride usually forms as a platelet, its orientation is important since cracking of circumferential hydride will not lead to failure of the tube whereas cracking of radial hydride could lead to through-wall cracks. In this regard, the texture of the zirconium alloy pressure tube is important since if one obtains the 'correct' texture, it becomes more difficult to reorient the hydride by stress. Also the direction of the stress with respect to the hydride plate is important both in terms of cracking and the ease with which the hydride can be reoriented. For the Zr-2.5 wt% Nb pressure tubes, Chinese work has demonstrated that hydrostatically extruded tubes are preferred to those extruded at high temperatures by conventional means since it is more difficult to reorient the hydride in a radial orientation in the hydrostatically extruded tubes.

There appears to be the need for more work on control of hydride orientation/reorientation by control of texture. In this regard, there is probably a need to characterize the texture of materials in a more precise fashion than by the use of basal (or other) pole figures which only characterize the texture with respect to 2 axes. In the in-reactor deformation area, the need for a three-axis representation of texture has been recognized and the CODF (Crystallite Orientation Distribution Function) is being recommended. This approach should probably be taken considering the DHC problem. Furthermore, there is evidence in the literature for Zr-2.5 wt% Nb and Excel Alloy (Canadian sources but non-AECL/OH) that as the hydrogen concentration is increased there are more radially oriented hydrides formed even in non-stressed specimens. This could be of concern if general hydrogen levels become high after long in-reactor exposure times. Radial hydrides have been seen in Zr-1 wt% Nb fuel cladding irradiated to high fluences; these hydrides were associated with areas of localized high corrosion.

The DHC phenomenon has two stages, initiation and propagation. Most of the published information concerns crack propagation. The initiation stage would seem to require a defect (small crack, scratch, etc.) to be present or to be produced by localized corrosion. Surface finish is of paramount importance, as has been shown in Russian work, since poor surface finish can either immediately provide the crack initiation or can lead to localized corrosion which then provides the initiation. All factors which lead to localized corrosion are obviously important in controlling the ease of initiation of DHC. This again would include the effects of second-phase particles and crevice corrosion.

There is little data available on the effects of irradiation on DHC. Russian work on Zr-2.5 wt% Nb has shown that irradiation led to a reduction in the maximum degree of reorientation that could be produced by imposition of a tensile stress. This reduction in degree of reorientation is considered to be due to the fact that irradiation reduces the effective solubility of hydrogen in zirconium (the hydride must first dissolve in order to reprecipitate in a new orientation). The crack velocity during propagation is related to, among other factors, the product of the diffusion coefficient (D) and the terminal solid solubility (TSS). If indeed irradiation leads to a reduction in TSS, then the crack velocity should also be reduced. Also, since diffusion of H is by an interstitial mechanism, irradiation should lead to trapping and a reduction in D and hence a reduction of crack velocity. Thus we may conclude that under irradiation, the hydrides should be more difficult to reorient and even if they do reorient and crack, crack propagation rates should be slower than in unirradiated material.

I. FINAL OVERVIEW

Most of the world literature we have accessed leads to the conclusion that fuel channels having Zr-2.5 wt% Nb pressure tubes should perform satisfactorily with respect to degradation from corrosion and hydriding provided they are installed correctly and do not operate under conditions that are far removed from those expected by design.

There is a distinct lack of long term data regarding corrosion and hydriding of Zr-2.5 wt% Nb and there is a concern that at very long service life there could be a 'breakaway' in oxidation and hydrogen acquisition similar to that seen in the Zircaloys. Furthermore, there is the potential of accelerated hydriding due to galvanic coupling or localized corrosion at crevices and/or second phase particles. The nature and effects of second phase particles are not well documented, and there appears to be a need for studies that relate not only to pressure tubes but also to other zirconium alloy structural components. In this regard there may be a need to revise material specifications to allow for greater control of the impurity contents if such impurities are identified as a source of variability in structures and properties.

Looking at pressure tubes in general one is reminded of the fact that no two tubes are exactly the same since they all have minor differences in chemistry, structure and operating conditions in-reactor. The differences in structure are even evident as one goes from the front end to the back end of an individual tube. Given all these minor differences, it is not surprising that in-reactor data on corrosion and hydriding shows a large amount of scatter and general trends are difficult to detect and model. Greater effort seems required on the metallurgical characterization of the pressure tubes and the relationship between structure and properties such as corrosion and hydriding.

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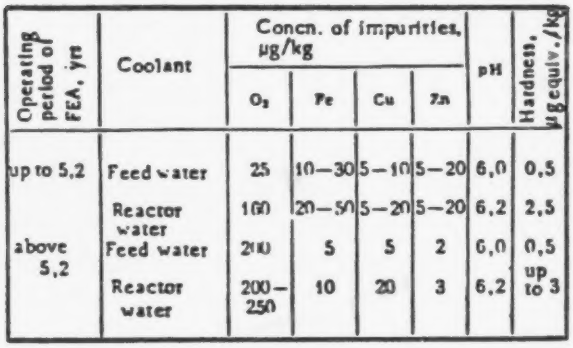
TABLE I : Characteristic Data of Some German Reactors.
(Garzarolli et al , ref.4)

Reactor	System	System Pressure, bar	Average Linear Heat Generation rate, W/cm	Max Fast Neutron Flux, n/cm^2 s	Water		Chemistry	
					O_2, ppm	H_2, ppm	Li, ppm	B, ppm
Obrigheim (KWO)	PWR	145	177	9×10^{13}	$\lesssim 0.005$	2 to 4	1 to 2	2000 to 0
Stade (KKS)	PWR	155	193	1.0×10^{14}	$\lesssim 0.005$	2 to 4	1 to 2	2000 to 0
Borselle (KCB)	PWR	155	203	1.1×10^{14}	$\lesssim 0.005$	2 to 4	1 to 2	2000 to 0
Biblis-A (KWB)	PWR	155	194	1.0×10^{14}	$\lesssim 0.005$	2 to 4	1 to 2	2000 to 0
Neckarwestheim (GKN)	PWR	155	226	1.5×10^{14}	$\lesssim 0.005$	2 to 4	1 to 2	2000 to 0
Kahl (VAK)	BWR	70	125	4×10^{13}	2	stoichiometrically	...	...
Gundremmingen (KRB)	BWR	70	177	6×10^{13}	0.2		...	...
Lingen (KWL)	BWR	70	166	6×10^{13}	3		...	...
Würgassen (KWW)	BWR	70	230 (180)[a]	8×10^{13}	0.2		...	...

[a] For 8 by 8 type fuel bundles, the main part of the core consists of 7 by 7 bundles.

TABLE II : Water Chemistry of Coolant of the VK-50 Reactor.
(Tsykanov et al , ref.10)



Operating period of FEA, yrs	Coolant	Concn. of impurities, µg/kg				pH	Hardness, µg equiv./kg
		O_2	Fe	Cu	Zn		
up to 5,2	Feed water	25	10—30	5—10	5—20	6,0	0,5
	Reactor water	100	20—50	5—20	5—20	6,2	2,5
above 5,2	Feed water	200	5	5	2	6,0	0,5
	Reactor water	200—250	10	20	3	6,2	up to 3

TABLE III : Composition of Zirconium Alloys

WEIGHT %

ELEMENTS	ZRY-1	ZRY-2	ZRY-3	ZRY-4	ZR-1NB	ZR-2.5NB	VALLOY S	OZHENNITE	EXCEL	GARTER SPRING
Sn	2.5	1.20-1.70	0.25	1.20-1.70				0.2	3.5	
Fe		0.07-0.20	0.25	0.18-0.24			0.28	0.1		0.15max.
Cr		0.05-0.15		0.07-0.13						
Ni		0.03-0.08		....				0.1		
Fe+Cr+Ni		0.18-0.38		0.28-0.37						
Nb					1.0	2.40-2.80		0.1	0.8	2.40-2.80
O		0.1-0.14 0.12 TYP.		0.1-0.14 0.12 TYP.		0.09-0.13				0.08-0.13
		MAXIMUM IMPURITIES, WEIGHT %								
Al		0.0075		0.0075		0.0075				
B		0.00005		0.00005		0.00005				
C		0.027		0.027		0.027				
Cd		0.00005		0.00005		0.00005				
Co		0.002		0.002		0.002				
Cr		....		....		0.02				
Cu		0.005		0.005		0.005	1.2			0.5-0.7
Fe		....		....		0.15				
H		0.0025		0.0025		0.0025				
Hf		,010		,010		,010				
Mg		0.002		0.002		0.002				
Mn		0.005		0.005		0.005				
Mo									0.8	
N		0.0065		0.0065		0.0065				
Ni		....		0.007		0.007				
O		SPEC'D		SPEC'D		....				
Si		0.012		0.012		0.012				
Sn		....		....		0.005				
Ti		0.005		0.005		0.005				
U		0.00035		0.00035		0.00035				
W		0.01		0.01		0.01				

TABLE IV: Hydrogen pick-up by zirconium-niobium alloys in water at 350 C and 168 atm. (18,000 hr.exposure).
(Parfenov et al , ref.11)

Nb content.%	Corrosion hydrogen picked up, %
0	89
0.5	36
1.0	24
1.5	21

TABLE V : Chemical Composition of Some ZrNb test Alloys
(Beyer et al . ref.49)

melt no.	alloy	weight % Nb	weight ppm			
			O	N	H	C
1143/41	ZrNb 1	1.20	90	22	6	160
1143/40		0.82	65	16	10	190
1123/1		1.17	167	50	8	350
1161/18		0.95	28	71	5	293
1143/43	ZrNb 2.5	2.23	48	27	6	230
1143/43		2.79	43	25	8	200
1123/2		2.54	375	35	15	60
1143/31		2.33	99	18	5	340

TABLE VI : Corrosion Results of Differently Treated Welds.
(Tyurin et al , ref.59)

Test No.	Type of treatment	Condition of surface of specimens after corrosion testing for 3000hr
1	Welding without subsequent treatment	White film on weld and HAZ, black film on base metal (BM)
2	Welding + annealing at 550^{o}C, 10hr	White film on weld and HAZ, black film on base metal (BM)
3	Welding + burnishing	White film on weld and HAZ, black film on base metal (BM)
4	Welding + burnishing + annealing at 550^{o}C, 5hr	Black film on weld, HAZ and BM
5	Welding + burnishing + annealing at 550^{o}C, 10hr	Shiny black film on weld, HAZ and BM
6	Welding + volumetric cold deformation by 30, 50 and 75%	White film on weld and HAZ, black film on BM
7	Welding + deformation by 30% + annealing at 550^{o}C, 10hr	White film on HAZ, grey film on weld and BM
8	Welding + deformation by 50% + annealing at 550^{o}C, 10hr	Black film on weld and BM, grey film on HAZ
9	Welding + deformation by 75% + annealing at 550^{o}C, 10hr	Black film on weld, HAZ and BM

TABLE VII: Hydride Reorientation Threshold Stress of Tubes with Different Original Textures. (Jie et al , ref.80)

MATERIAL	TEXTURE CHARACTERISTIC of TUBE	POLE DENSITY		HYDRIDE REORIENTATION THRESHOLD STRESS MPa
		Tangential (1010)	Radial (0002)	
TUBE, hydrostatically extruded. H: 80 ppm	-radial basal pole texture (circumferential hydride)	0.38	4.56	400-550
TUBE, conventionally hot extruded & cold rolled H: 80 ppm	-circumferential basal pole texture (circumferential hydride)	6.89	0.46	260-330

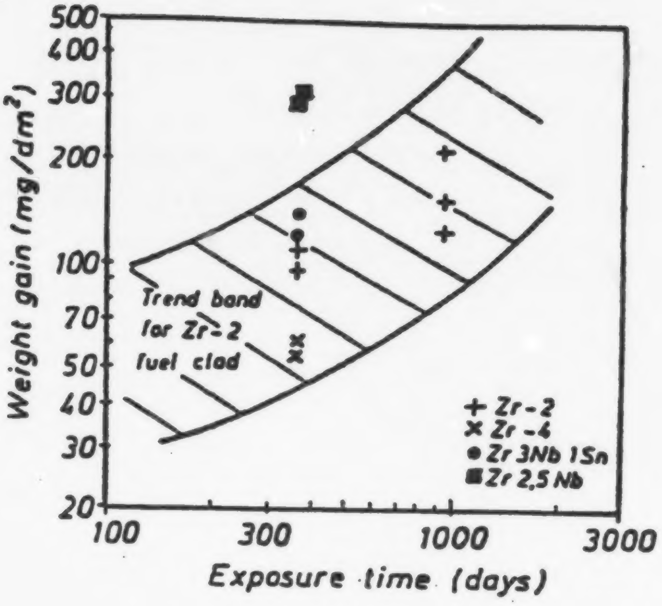


Figure 1: Weight Gain of Different Zirconium Alloys Over Exposure Time in BWR Environment. (Garzarolli et al , ref.3)

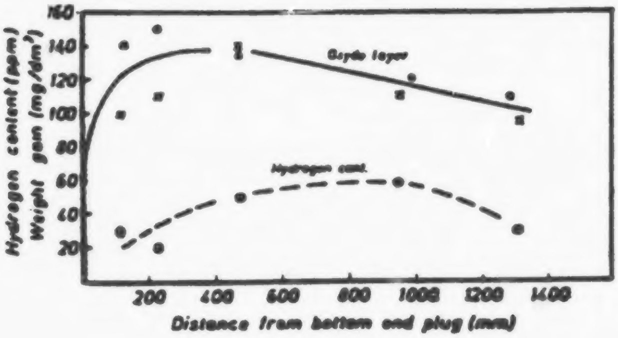


Figure 2: Weight Gain From Oxidation and Hydrogen Content Along VAK Element After 920 Days Irradiation. (Garzrolli et al , ref.3)

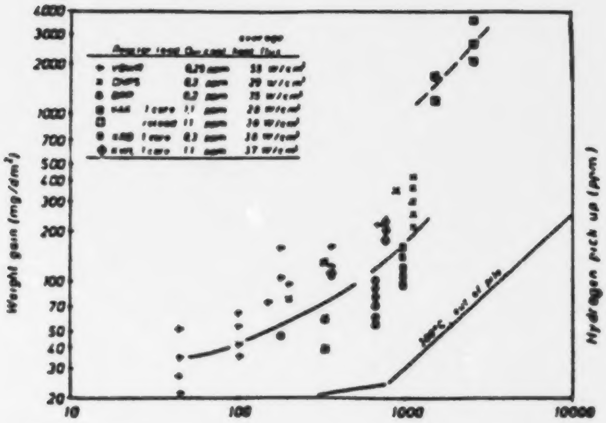


Figure 3: Results of Weight Gain vs Exposure Time in the Various German BWR's. (Garzarolli et al , ref.3)

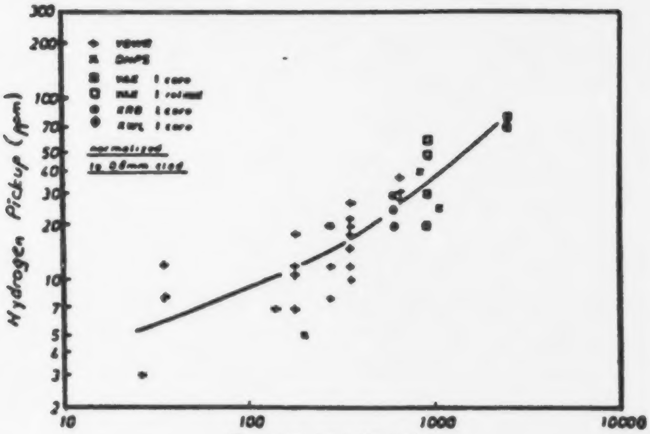


Figure 4: Hydrogen Pick-up vs Exposure Time From German BWR's. (Garzarolli et al , ref.3)

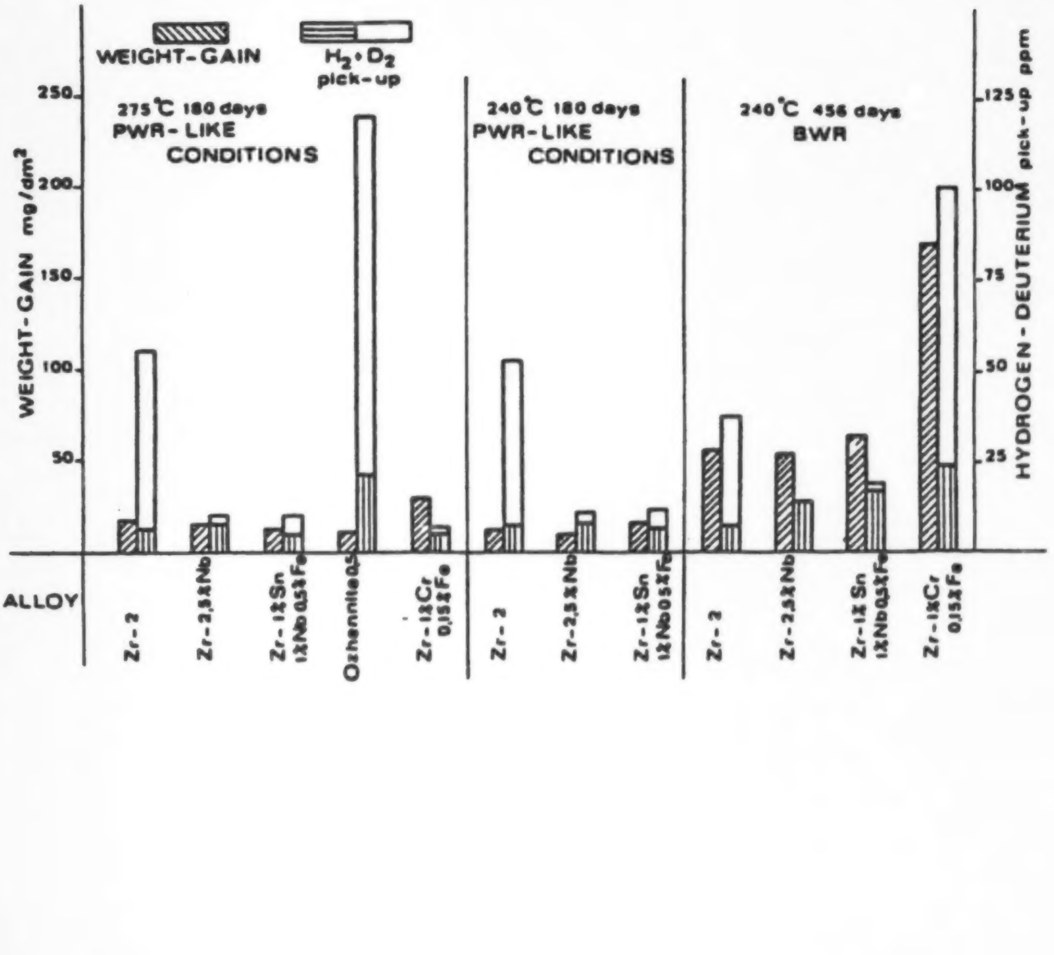


Figure 5: Hydrogen/Deuterium Pickup and Weight Gain of Zirconium Alloys Under Hydrogenated and Oxygenated Conditions. (Castaldelli et al , ref.6)

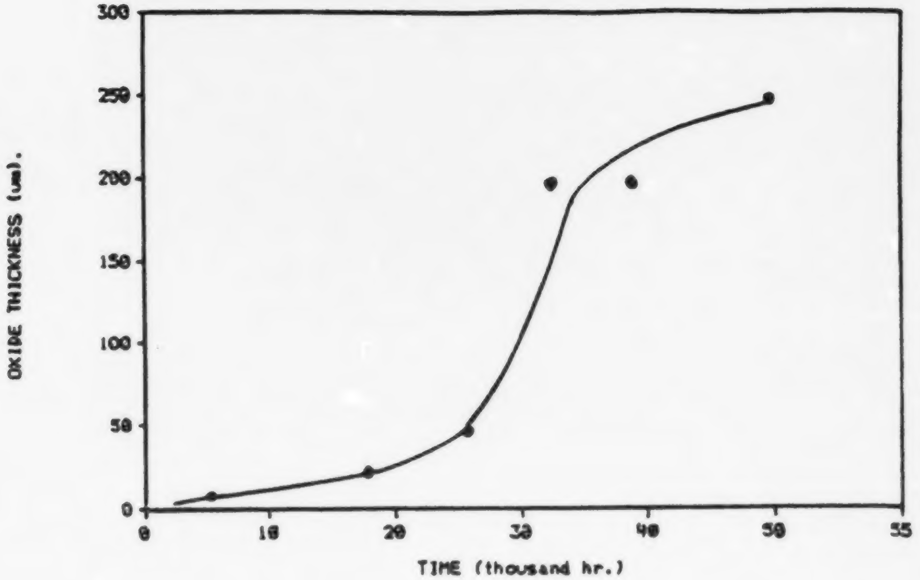


Figure 6: Variation in Maximum Thickness of Oxide Films on Fuel Element of the VK-50 Reactor. (Tsykanov et al , ref.10)

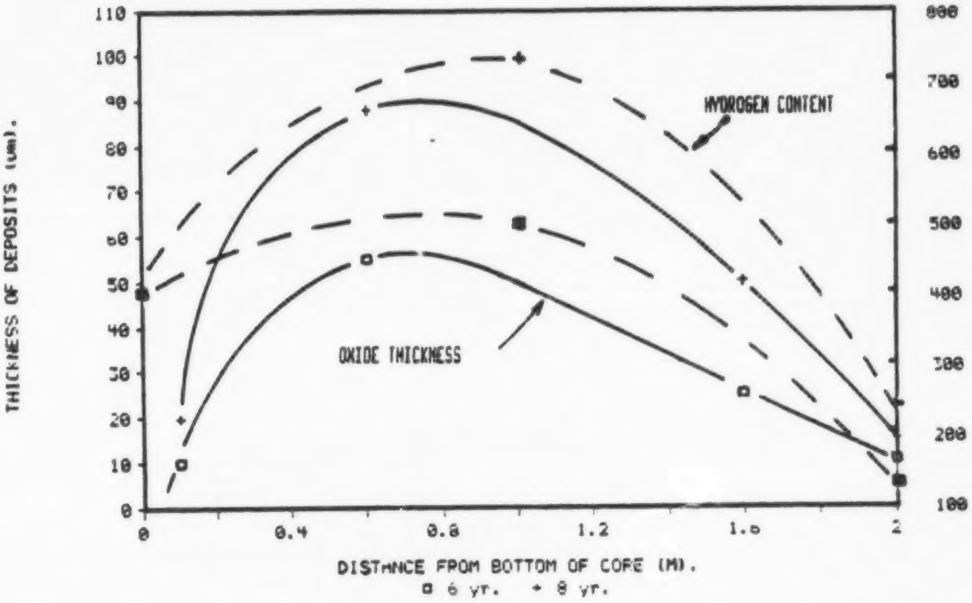
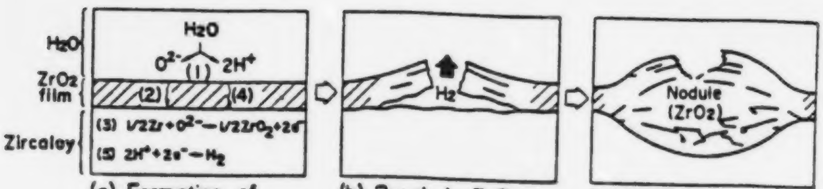


Figure 7: Oxide Thickness and Hydrogen Content Along Zr-1wt%Nb Cladding in VK-50 Reactor. (data from ref.10)


H2O
H2O
O2-
(1)
2H+
ZrO2 film
(2)
(4)
Zircaloy
(3) 1/2Zr+O2- — 1/2ZrO2+2e-
(5) 2H+ + 2e- — H2
H2
Nodule (ZrO2)

(a) Formation of ZrO_2 and H_2

(b) Break in ZrO_2 black film

(c) Formation of nodule

Figure 8: Mechanism of Zircaloy Nodular Corrosion. (Kuwae et al , ref.20)

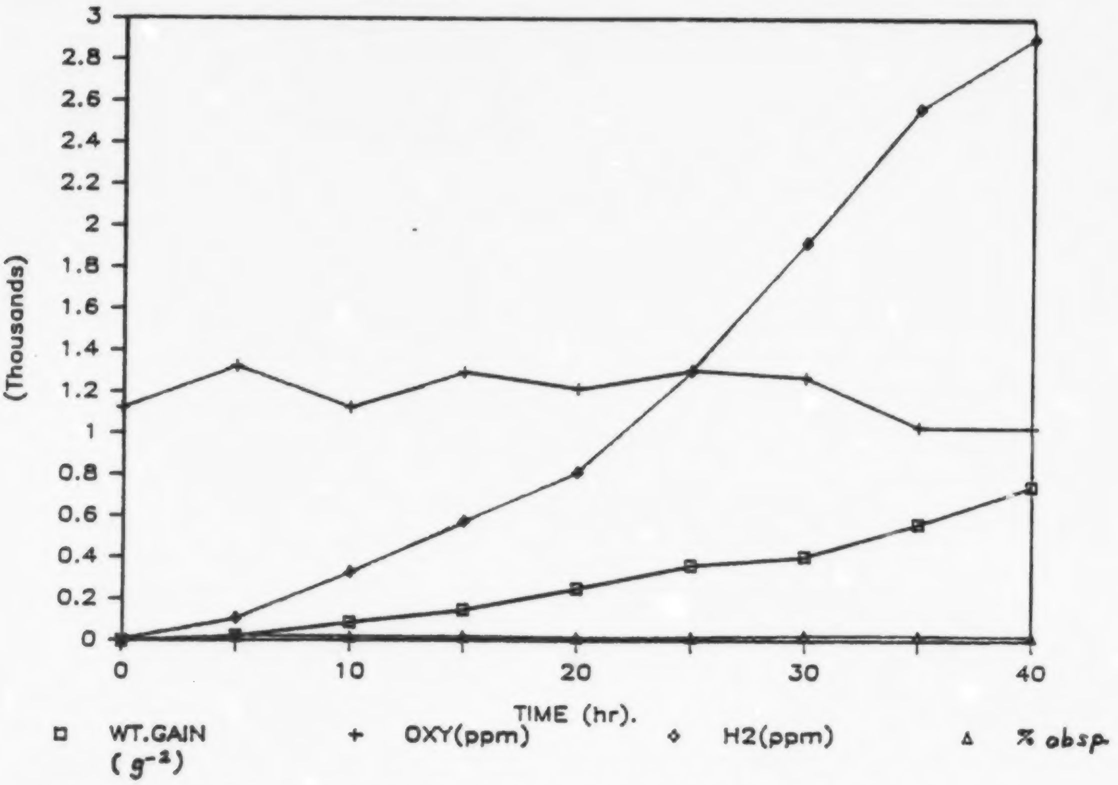


Figure 9: Weight Gains in Oxygen and Hydrogen During Nodular Corrosion of Zircaloy-4. (data from ref.20)

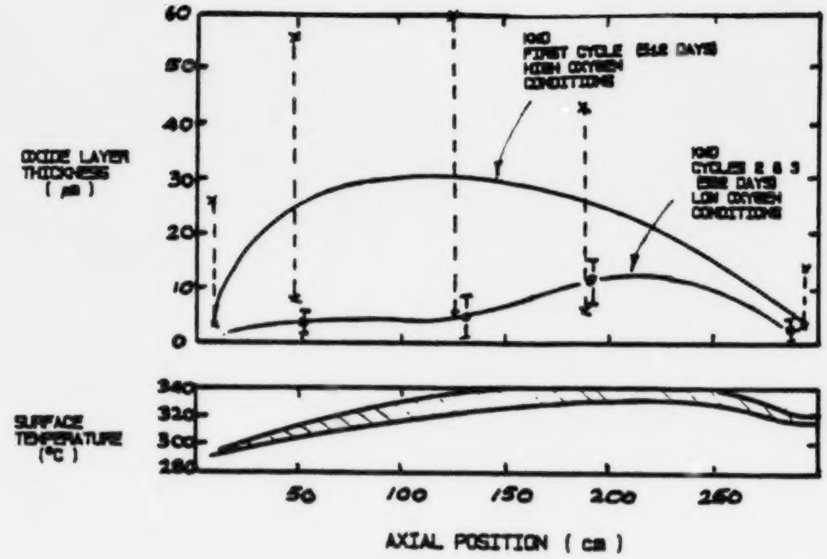


Figure 10: Oxide Thickness and Surface Temperature Along Fuel Rod Under Different PWR Coolant Conditions.
(Garzarolli et al , ref.33)

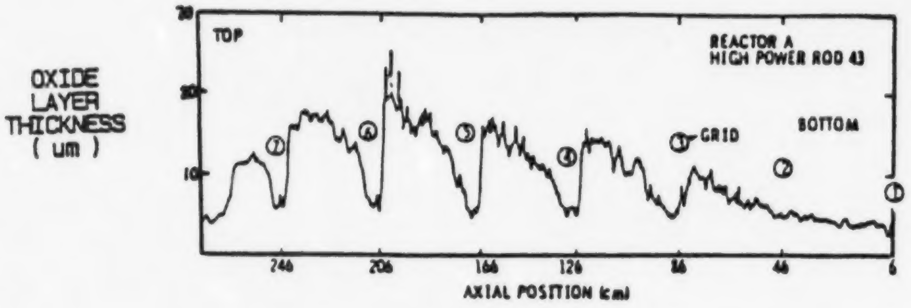


Figure 11: Typical Oxide Layer Thickness for a PWR Fuel Rod.
(Garzarolli et al , ref.33)

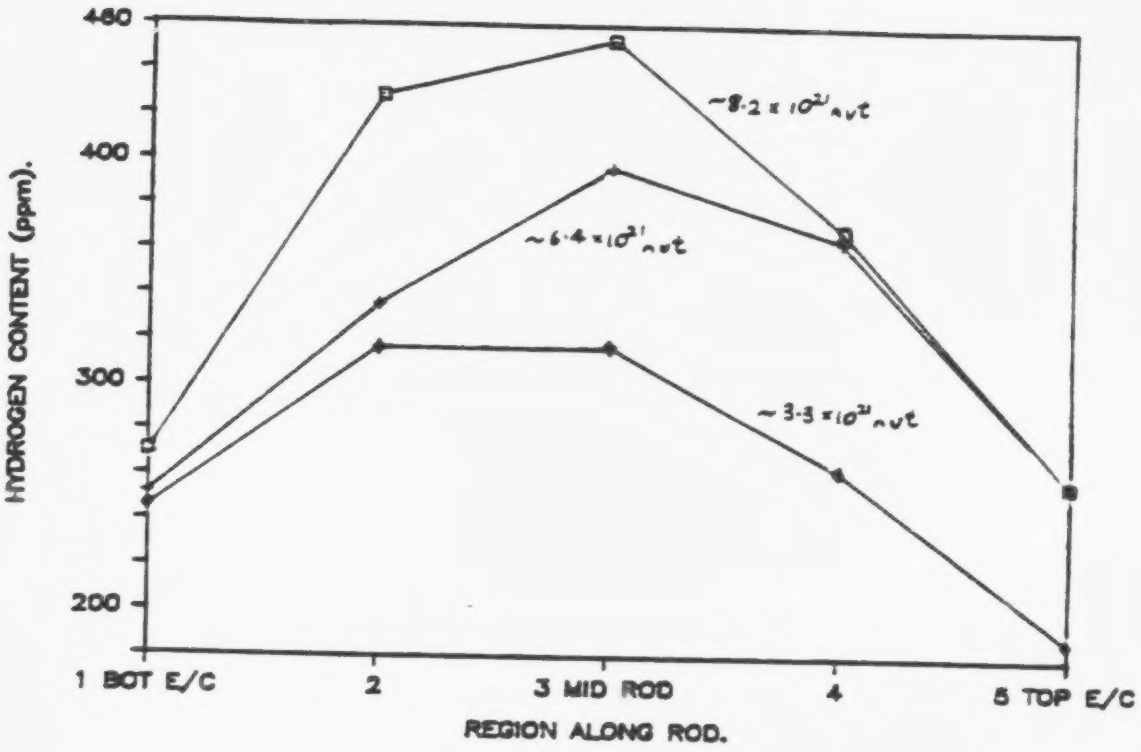


Figure 12: Hydrogen Distribution Along Zircaloy-2 Fuel Rod After 6300 Days Exposure in the Shippingport PWR Reactor. (data from ref.27)

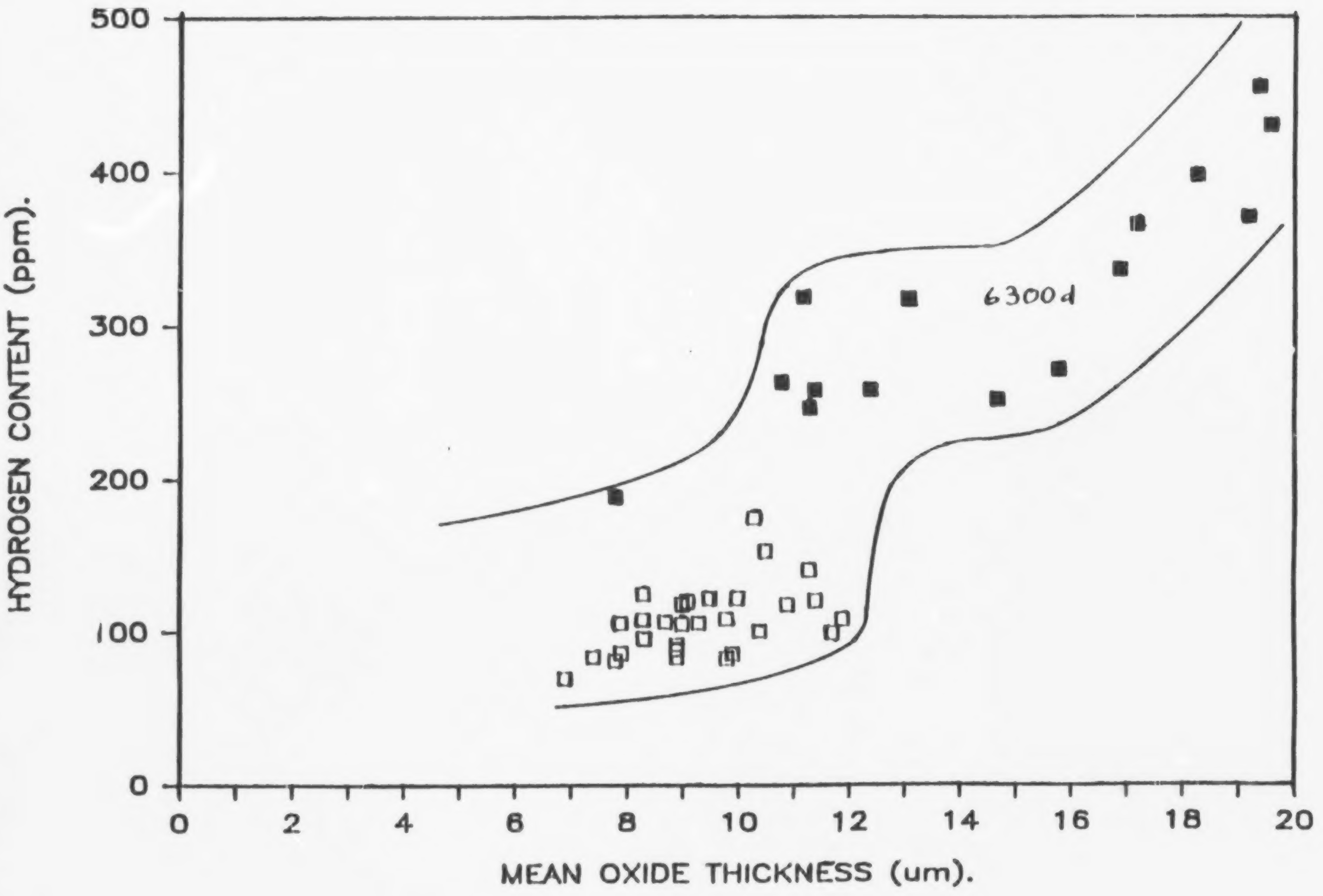
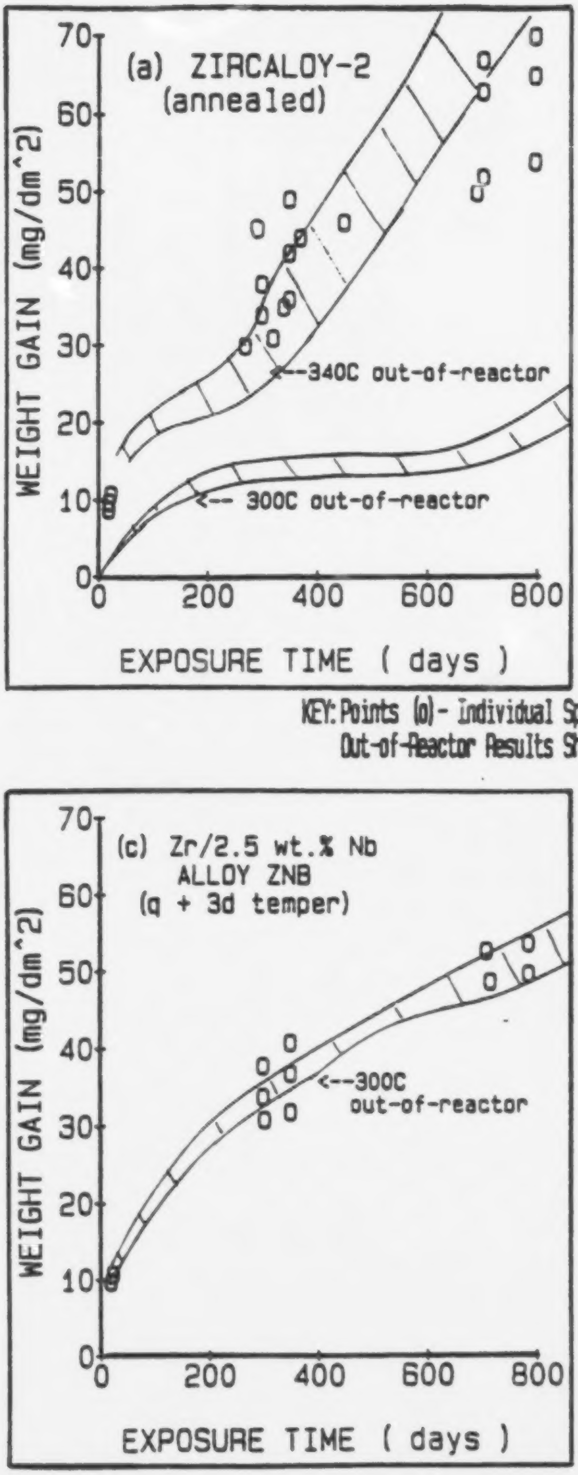


Figure 13: Variations in Hydrogen Content with Oxide Thickness of Zircaloy-2 Fuel Rod After 4100 and 6300 Days Exposure in the Shippingport PWR Reactor.
(data from ref. 26 & 27)



KEY: Points (o) - Individual Specimens In-Reactor at 300 C.
Out-of-Reactor Results Shown as Band or as Continuous Line.

Figure 14: Effect of Radiation on the Corrosion of Zircaloy-2 and Zr-2.5wt%Nb Alloy in Moist Carbon Dioxide-Air Mixture at 300°C. (Asher et al , ref.36)

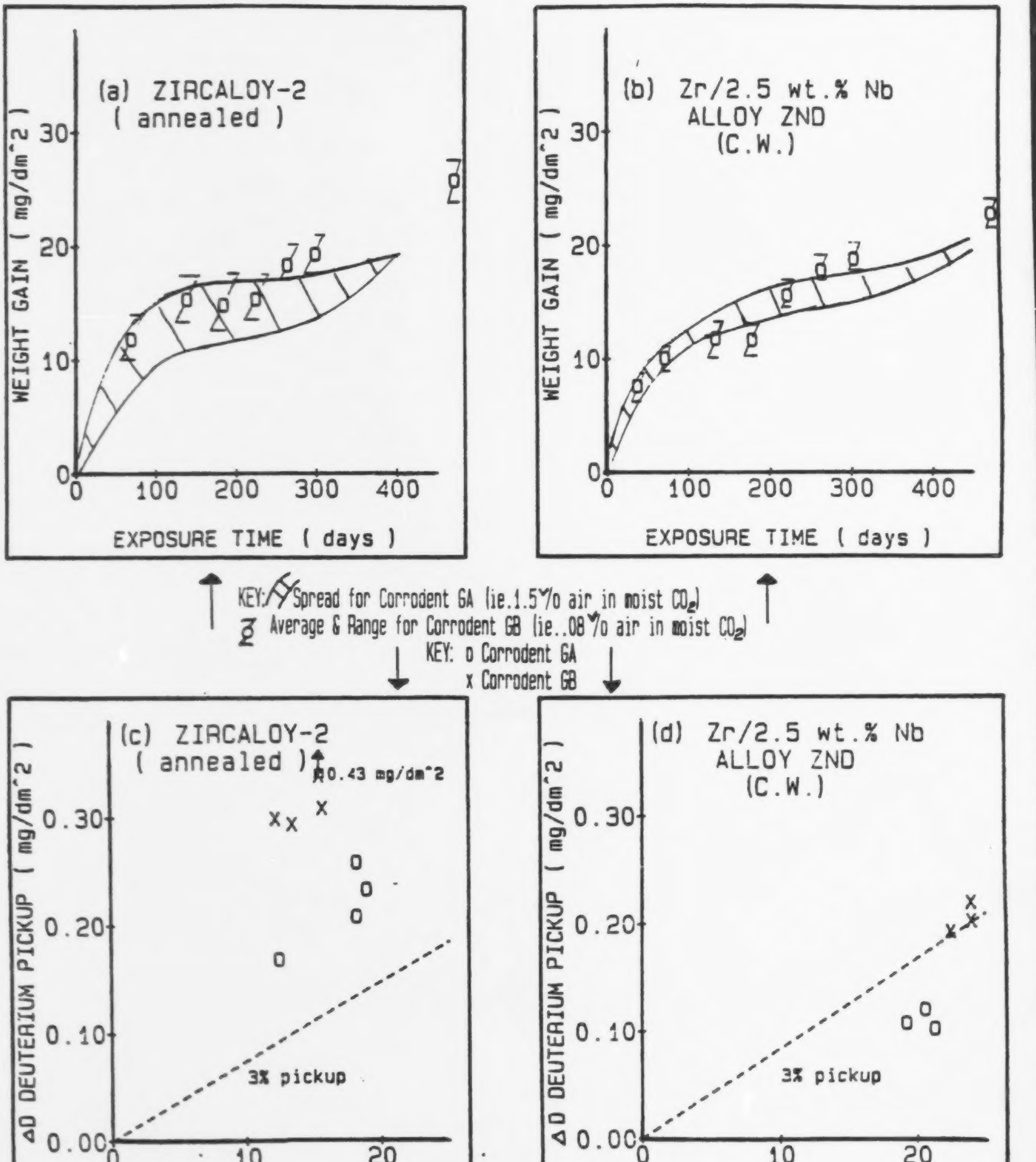


Figure 15: Effect of Corrodent Composition on the Corrosion and Hydrogen Pick-up of Zircaloy-2 and Zr-2.5wt%Nb Alloy in Moist Carbon Dioxide-Air Mixture in the Absence of Radiation. (Asher et al , ref.36)

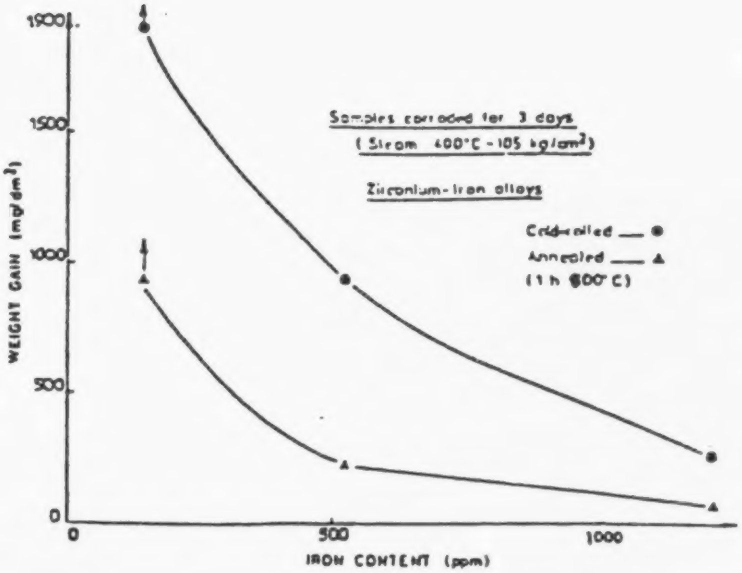


Figure 16: Effect of Iron on the Corrosion of Zirconium.
(Blanchet et al , ref.40)

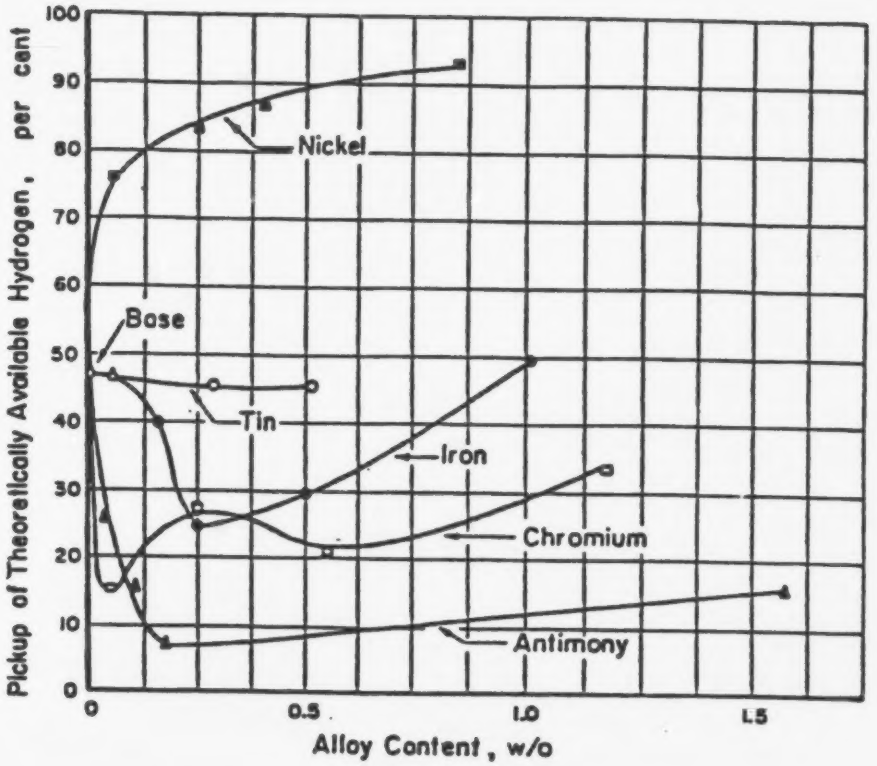


Figure 17: Hydrogen Absorption in Sponge-Base Zirconium Alloys Exposed up to 575 Days to 343 C Water. (Berry et al , ref.42)

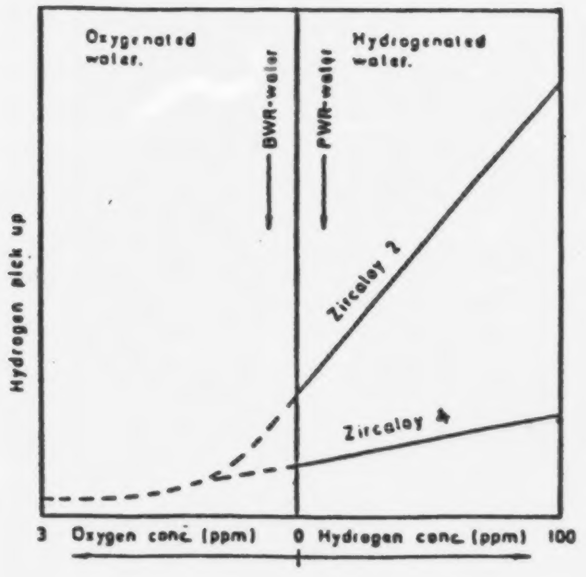


Figure 18: Out-of-Pile Absorption of Zircaloy-2 and -4 as a Function of Hydrogen and Oxygen Content in the Water Schematically. (Videm , ref.1)

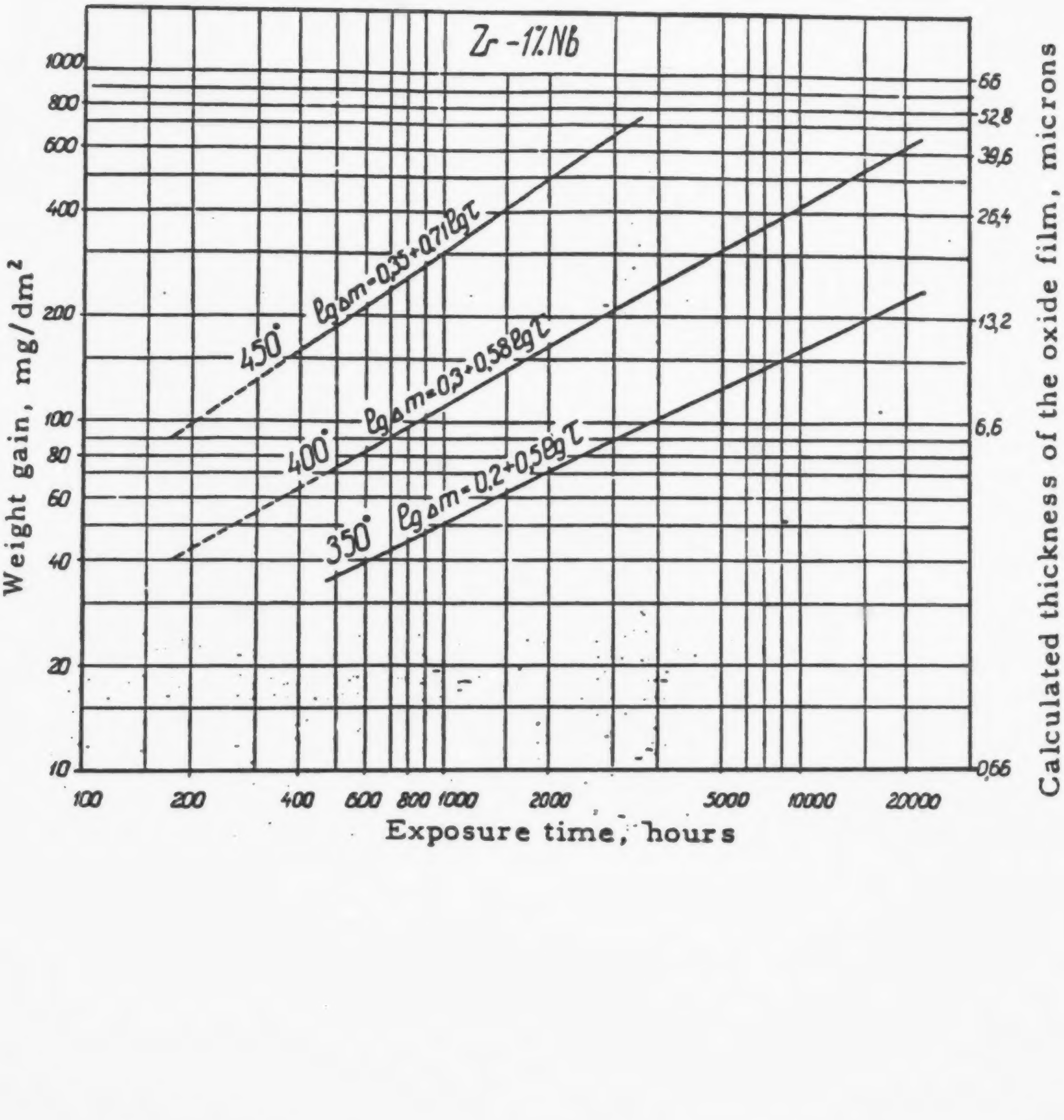


Figure 19: Corrosion of Zr-1wt%Nb in Water at 350°C - 17 MPa and in Steam at 400°C and 450°C - 30 MPa. (Kiselev et al , ref.45)

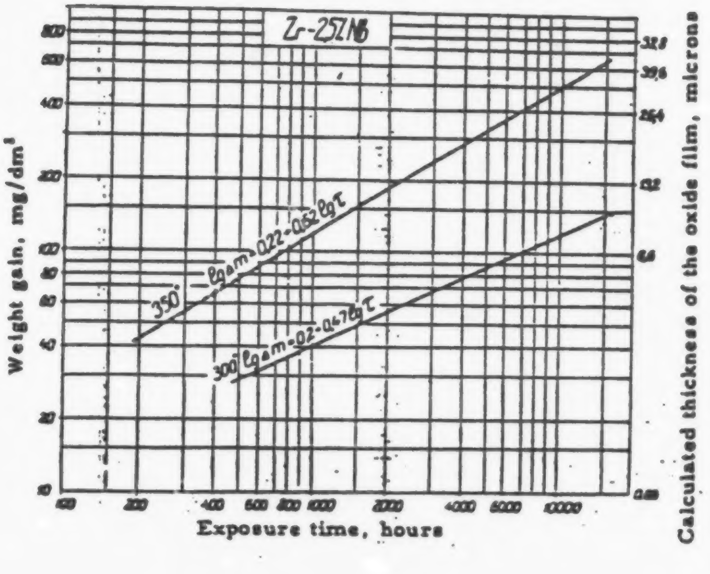
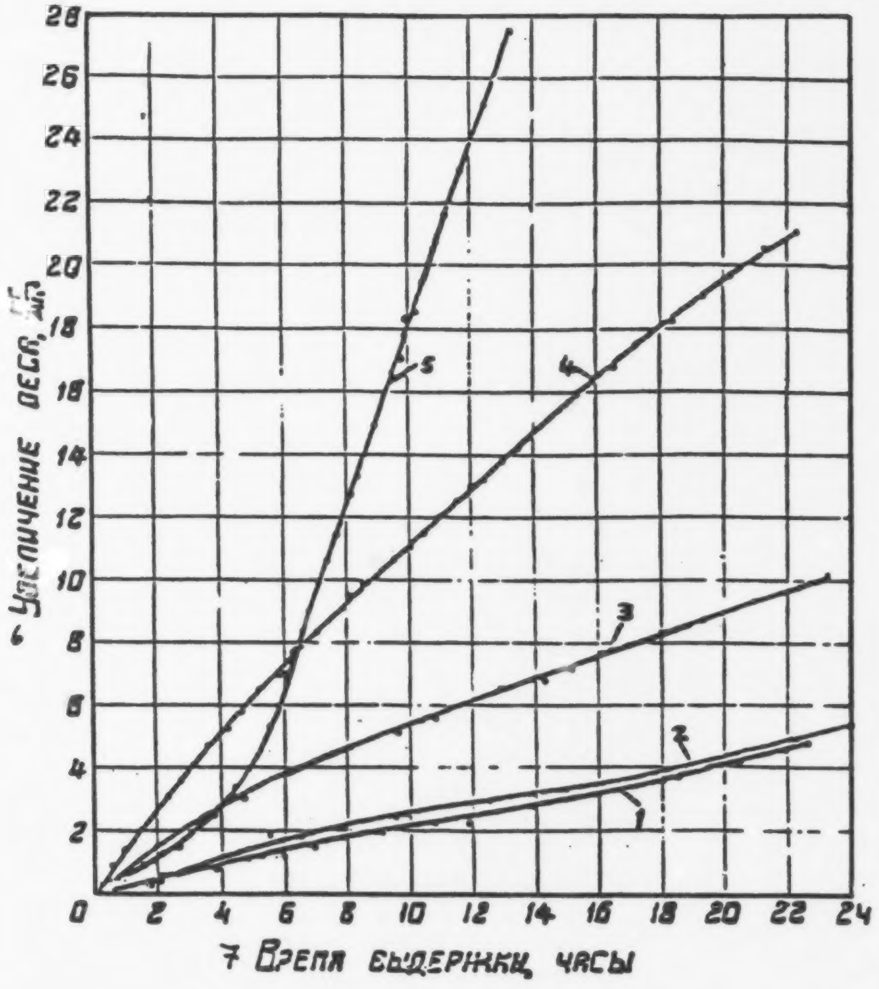


Figure 20: Corrosion of Zr-2.5wt%Nb in Water at 300°C - 9 MPa and at 350°C - 17 MPa. (Kiselev et al , ref.45)



1 1.0% Tin ; 0.2% Iron ; 0.3% Nickel
2 2.5% Niobium
3 1.0% Niobium
4 Iodide Zirconium (Heat 1073 . 0.002% Nitrogen)
5 Iodide Zirconium (Heat 1021 . 0.015% Nitrogen)
6 Weight Gain , mg/dm²
7 Exposure Time , hrs

Figure 21: Hydrogen Absorption by Zirconium and Its Alloys at 400C
(Ambartsumyam et al , ref.46)

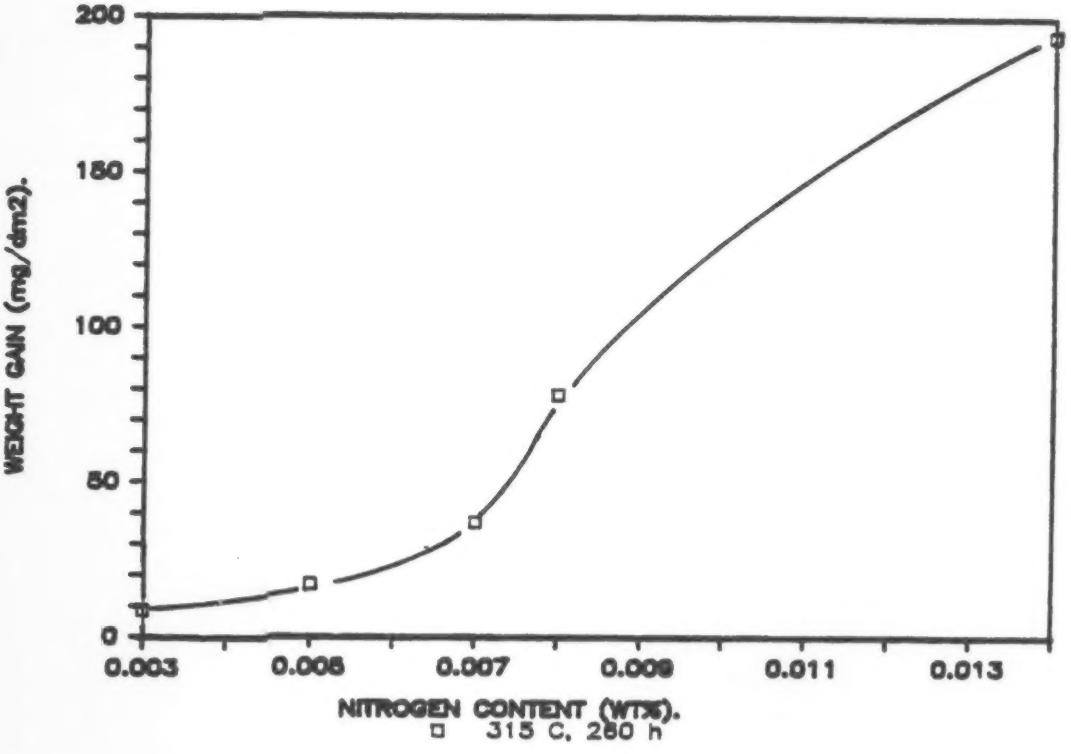


Figure 22: Effect of Nitrogen Level on the Corrosion Weight Gain of Zirconium. (data from ref.11)

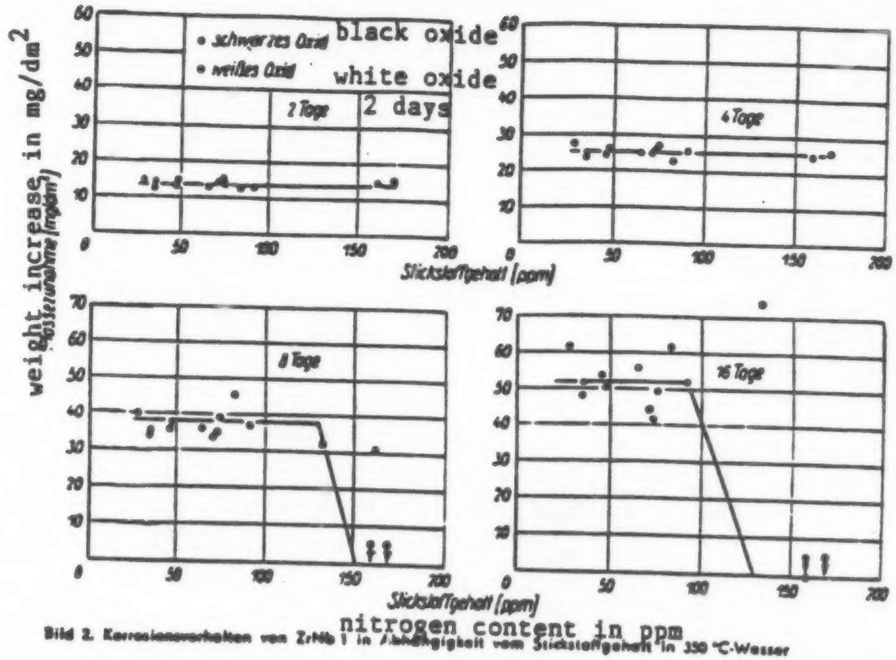


Bild 2. Korrosionsverhalten von ZrNb 1 in Abhängigkeit vom Stickstoffgehalt in 350 °C-Wasser

Figure 23: Corrosion Behaviour of Zr-1wt%Nb in 350 C Water as a Function of Nitrogen Content. (Huttig , ref.50)

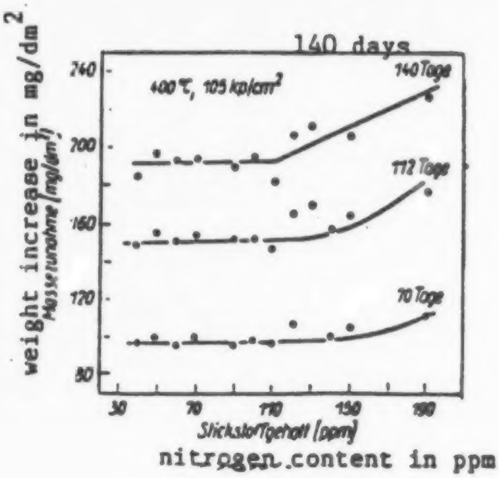


Figure 24: Effect of Nitrogen Content on the Corrosion Behaviour of Zircaloy-2. (Huttig , ref.50)

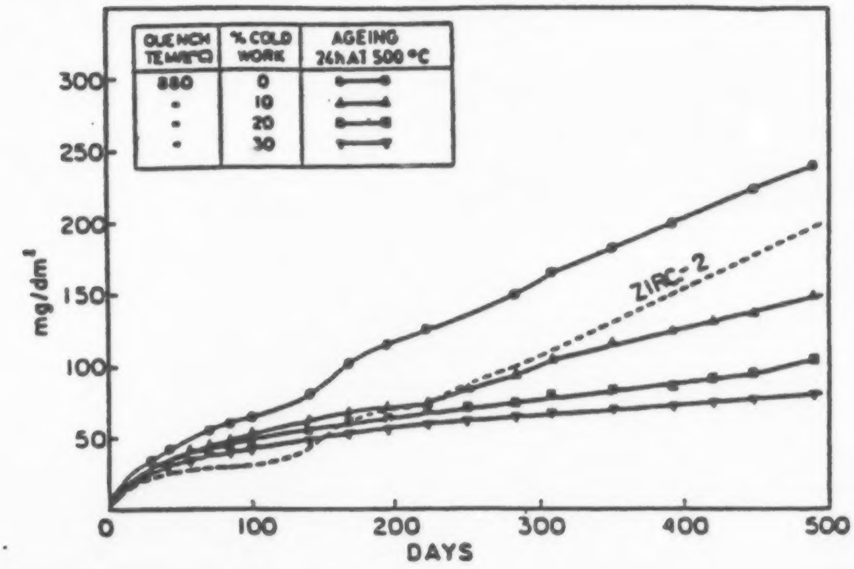


Figure 25: Effect of Cold Work and Ageing on the Corrosion of Zr-2.5wt%Nb in Water at 360 C. (LeSurf et al , ref.55)

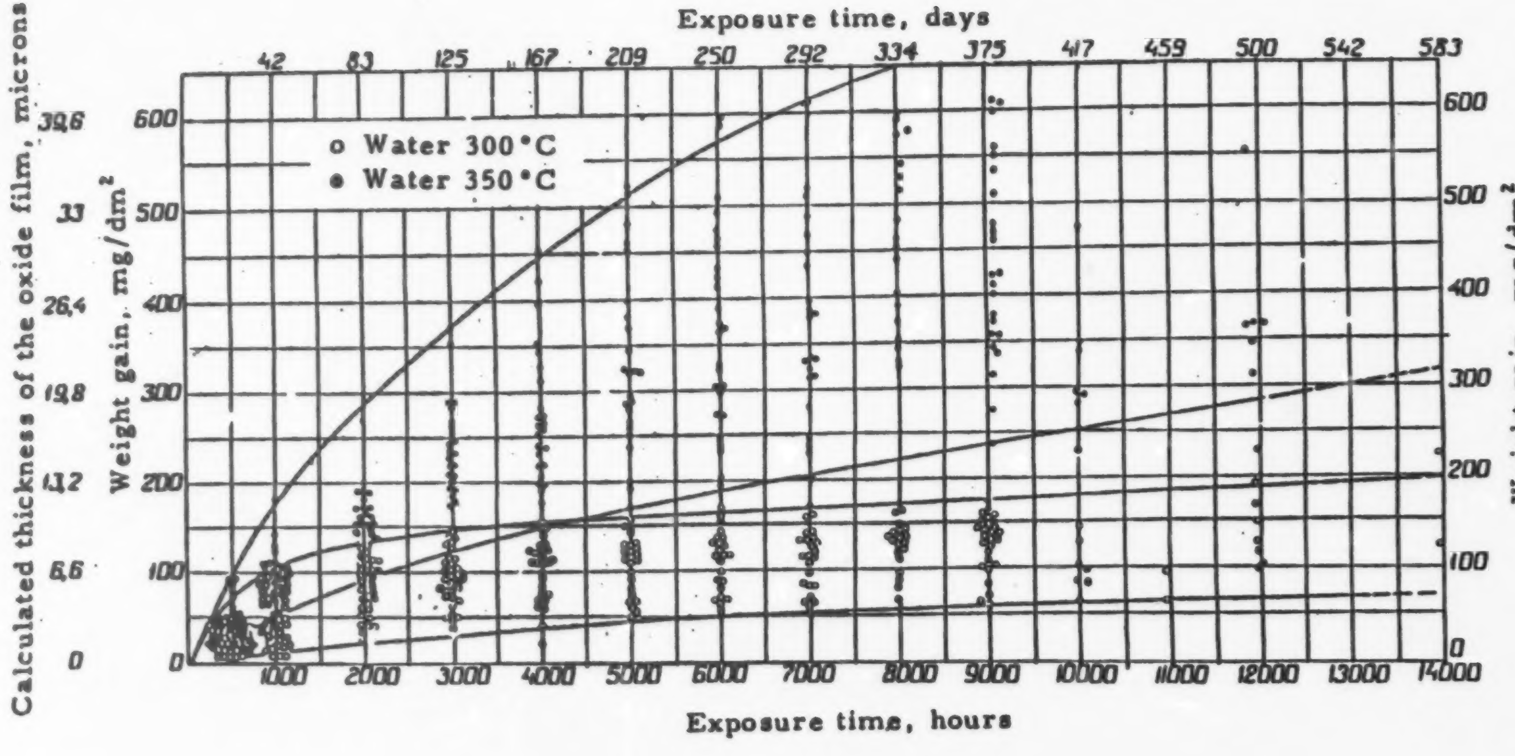
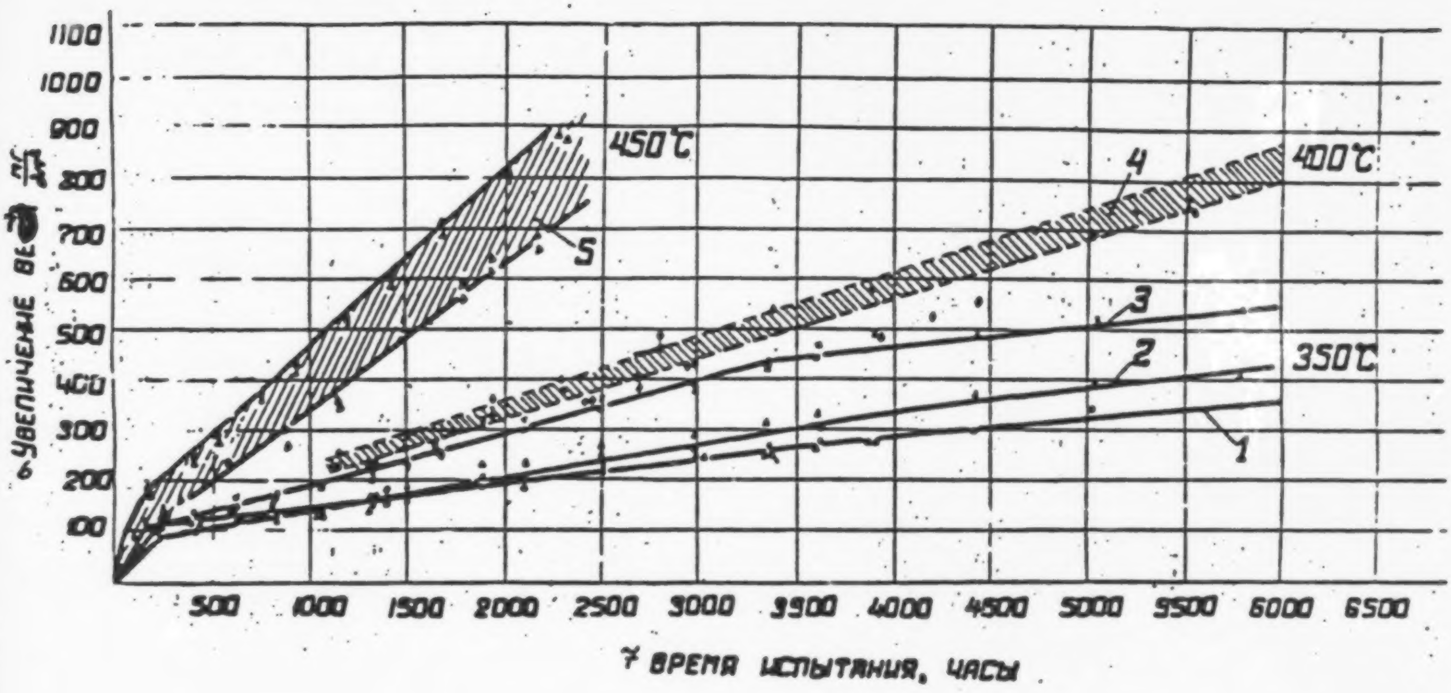


Figure 26: Corrosion of Zr-2.5wt%Nb in Water at 300 c - 9 MPa and at 350 C - 17 MPa. (Kiselev et al , ref.45)



1 2%-Niobium Alloy
2 2.5%-Niobium Alloy
3 5%-Niobium Alloy
4 2.5-3% Niobium Alloy
5 2.5-Niobium Alloy
6 Weight Gain, mg/dm^2
7 Exposure Time, hrs

Figure 27: Corrosion of Zr-Nb Alloys in Water and Superheated Steam at Various Temperatures.
(Ambartsumyam et al . ref.46)

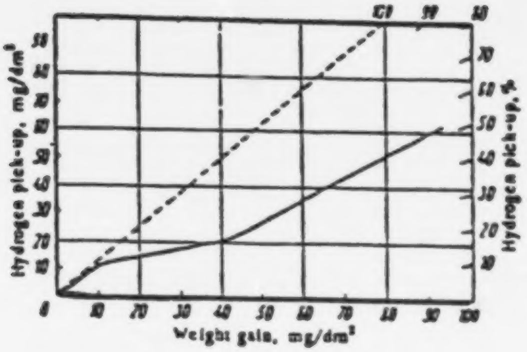


Figure 28: Hydrogen Pick-up by Zircaloy-2 as a Function of the Degree of Oxidation. (Parfenov et al , ref.11)

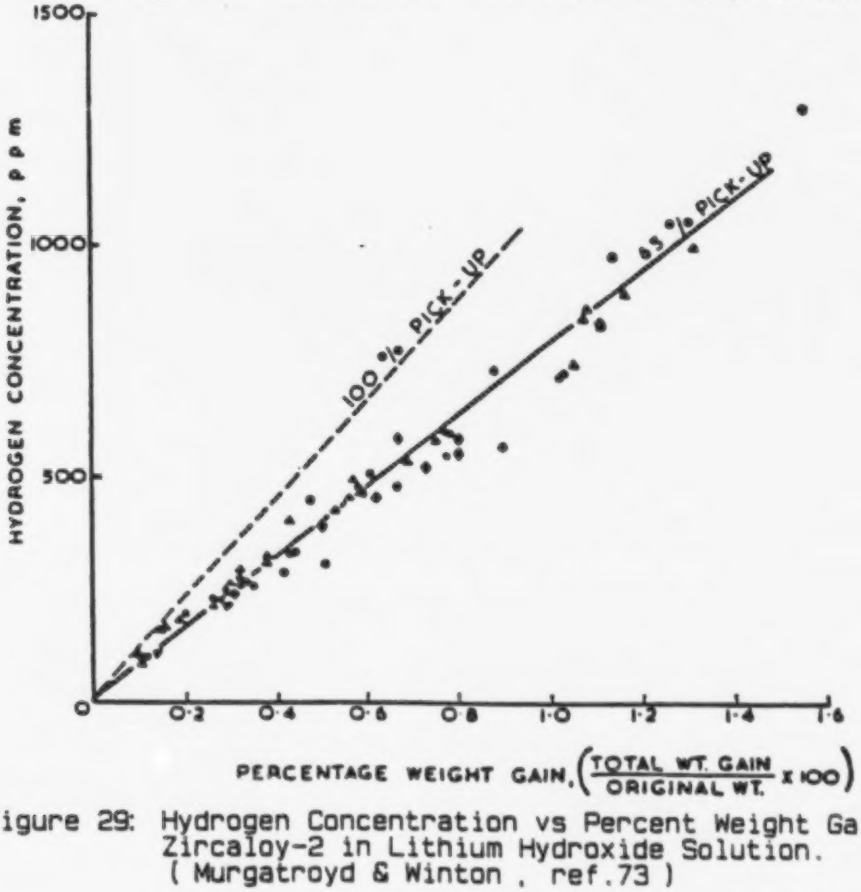
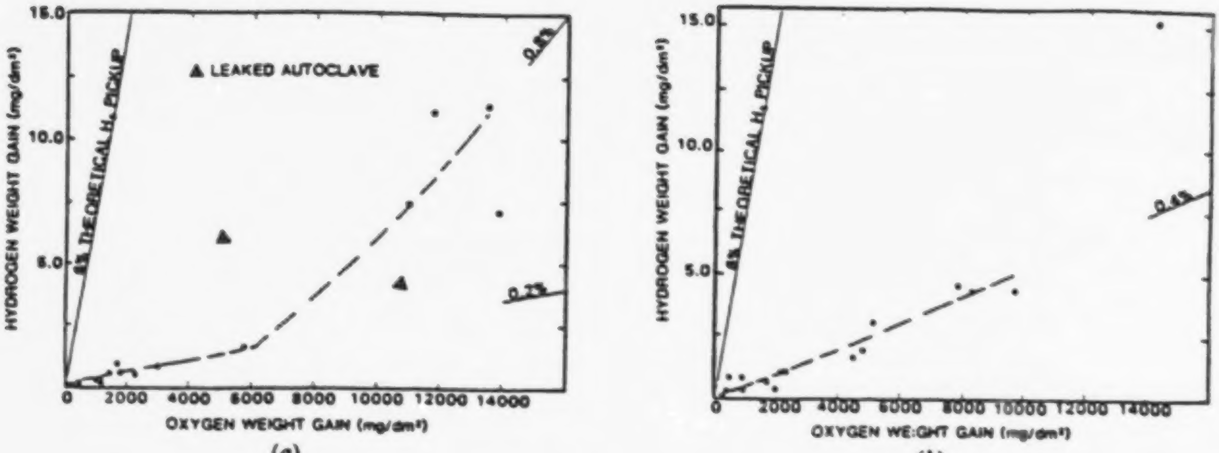
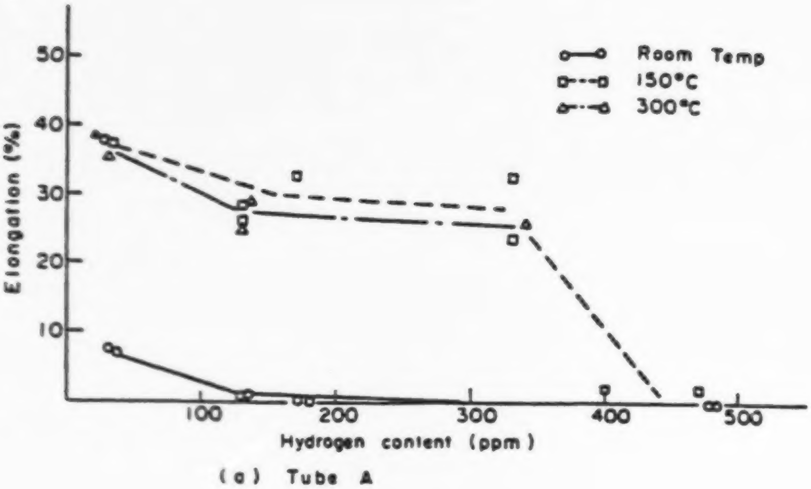


Figure 29: Hydrogen Concentration vs Percent Weight Gain of Zircaloy-2 in Lithium Hydroxide Solution. (Murgatroyd & Winton , ref.73)

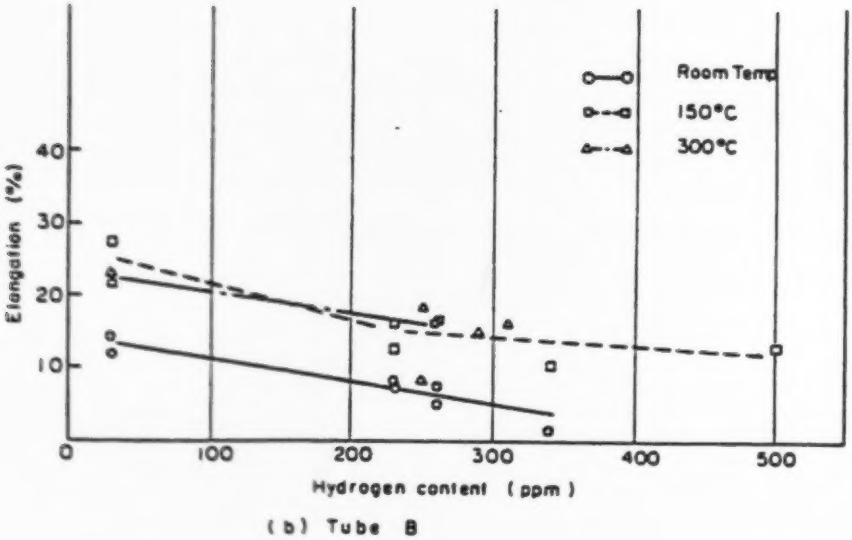


(a) (b)

Figure 30: Hydrogen Weight Gain vs Oxygen Weight Gain in Zr-2.5wt%Nb Alloy. (a) Cold Worked 40% (b) Heat-treated at 850 C and Aged 5 hr. at 560 C. (Zreiba & Northwood , ref.74)



(a) Tube A



(b) Tube B

Figure 31: Variation of Ductility of Zircaloy-2 Tube with Hydrogen Content. (Obara , ref.82)

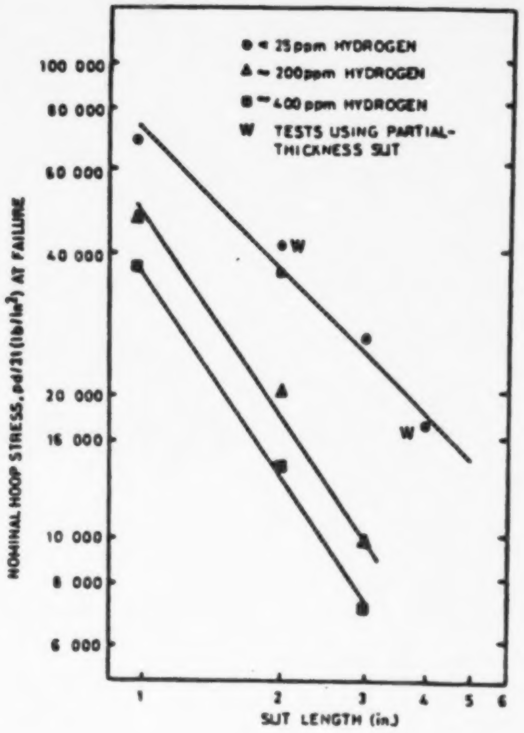


Figure 32: Effect of Slit Length on Nominal Failure Stress of Zircaloy-2 Pressure Tubes at 20 C.
(Cowan & Cowburn , ref.85)

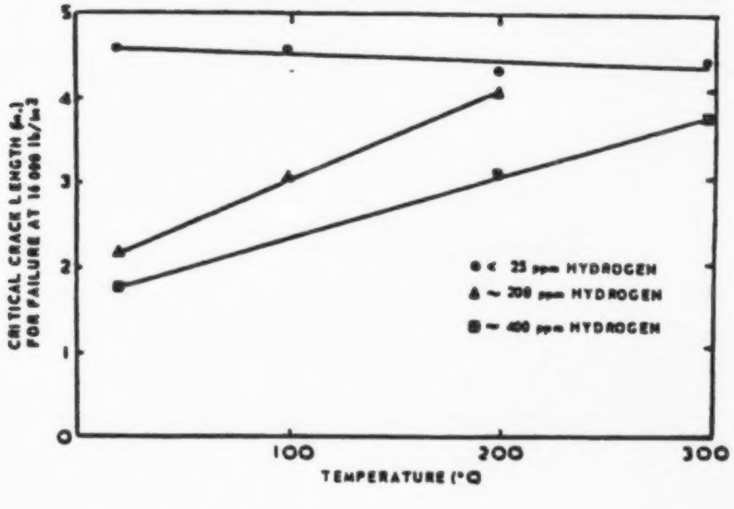


Figure 33: Effect of Temperature and Hydrogen Content on the Critical Crack Length Under a Hoop Stress.
(Cowan & Cowburn , ref.85)

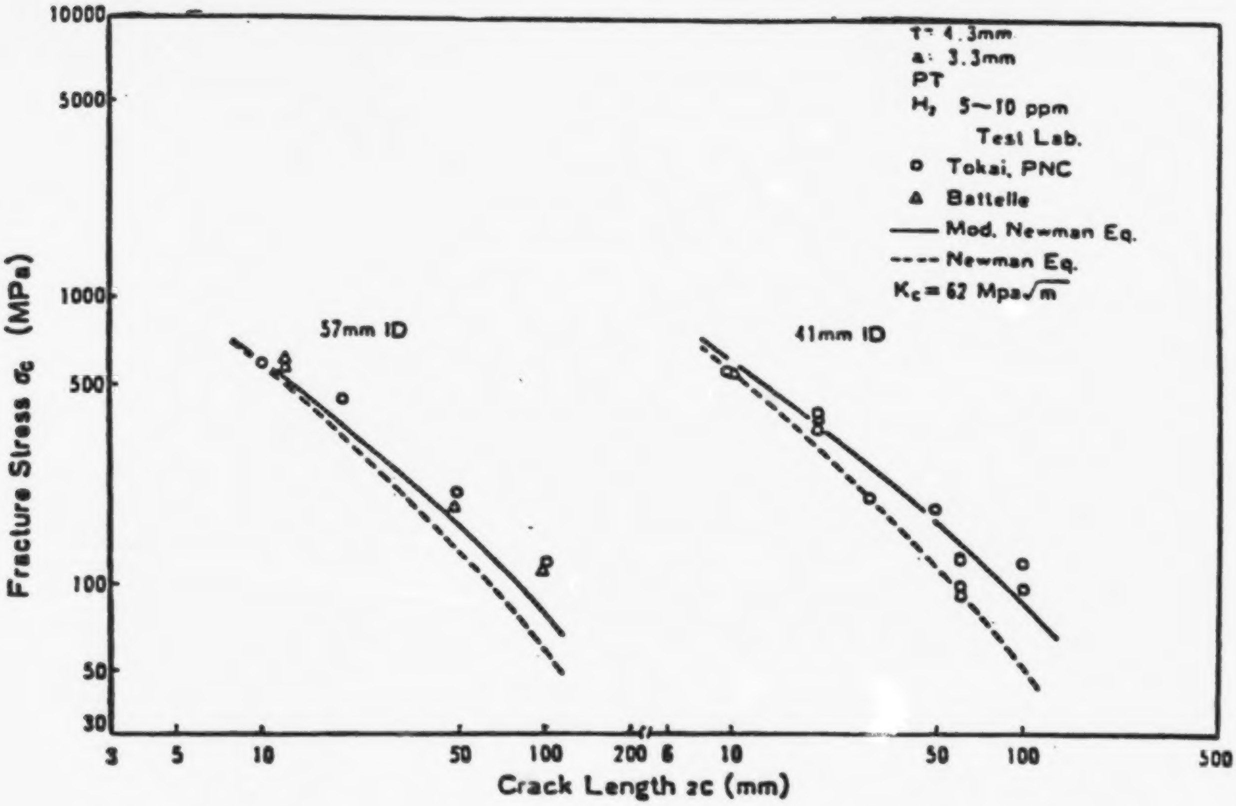


Figure 34: Burst Test Results of 41 mm ID and 57 mm ID Zr-2.5wt%Nb Tubes with Notches of 3.3 mm Deep.
(Honda et al , ref.89)

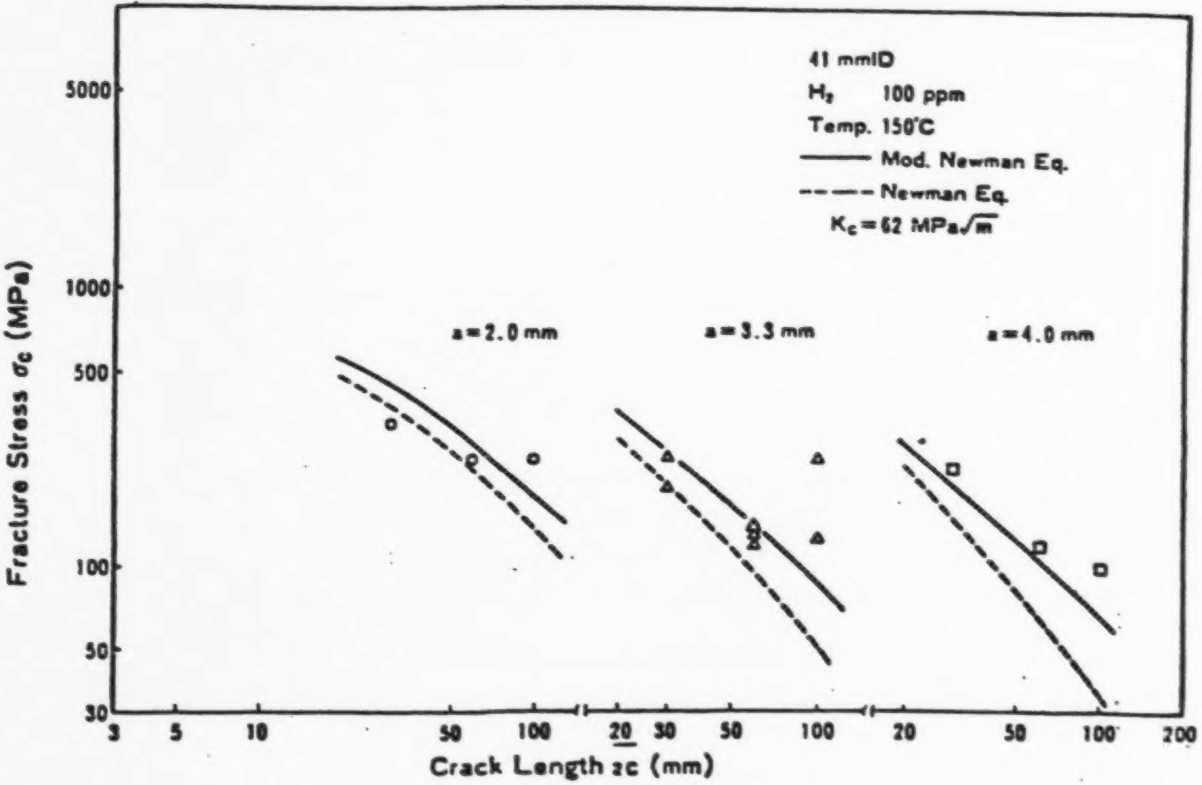


Figure 35: Burst Test Results of Zr-2.5wt%Nb Tubes Containing 100 ppm H_2 Tested at 150°C. (Honda et al , ref.89)

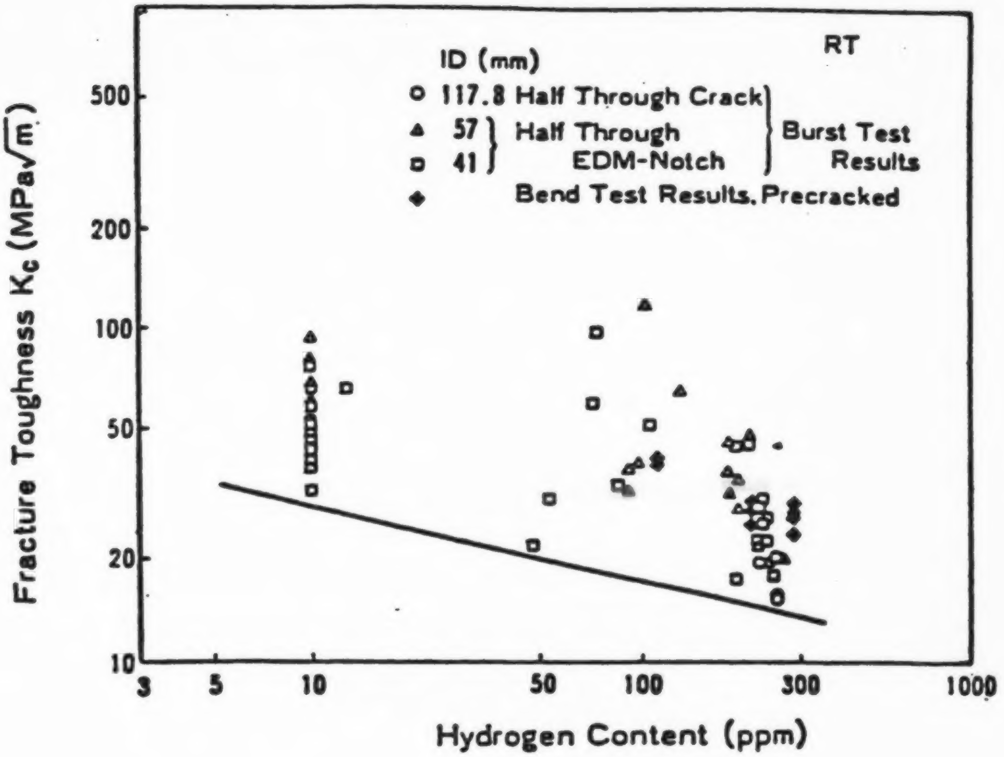


Figure 36: Comparison of Bend and Burst Test Results of Zr-2.5wt%Nb at Room Temperature. (Honda et al , ref.89)

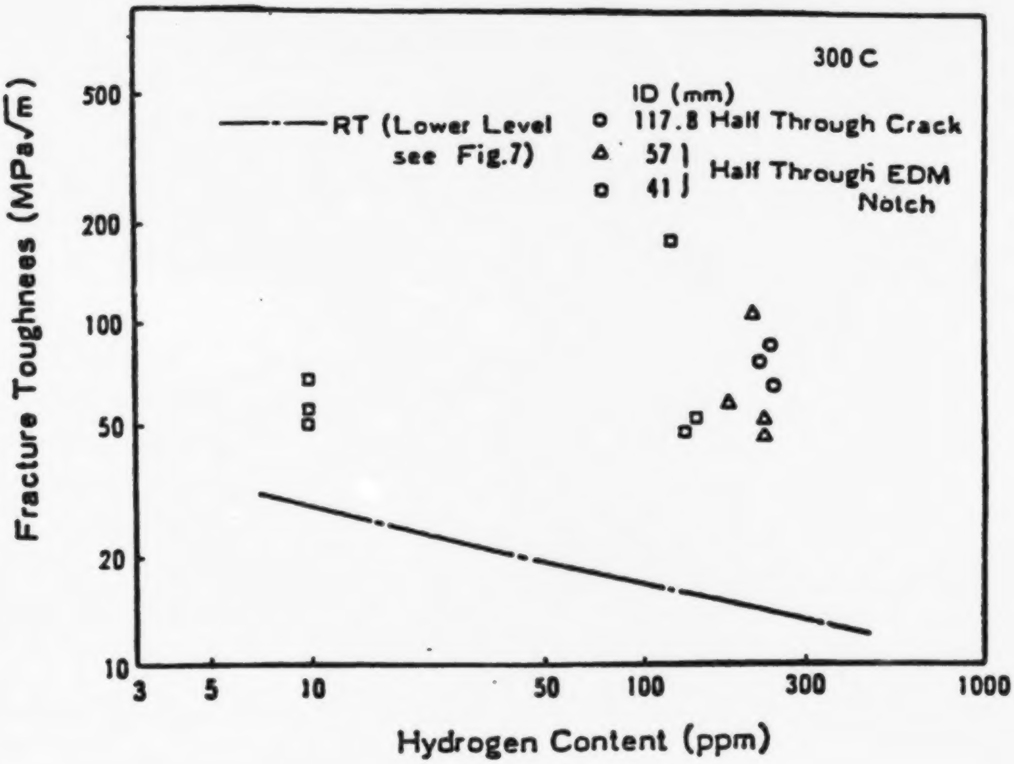


Figure 37: Fracture Toughness of Zr-2.5wt%Nb at 300 C.
(Honda et al , ref.89)

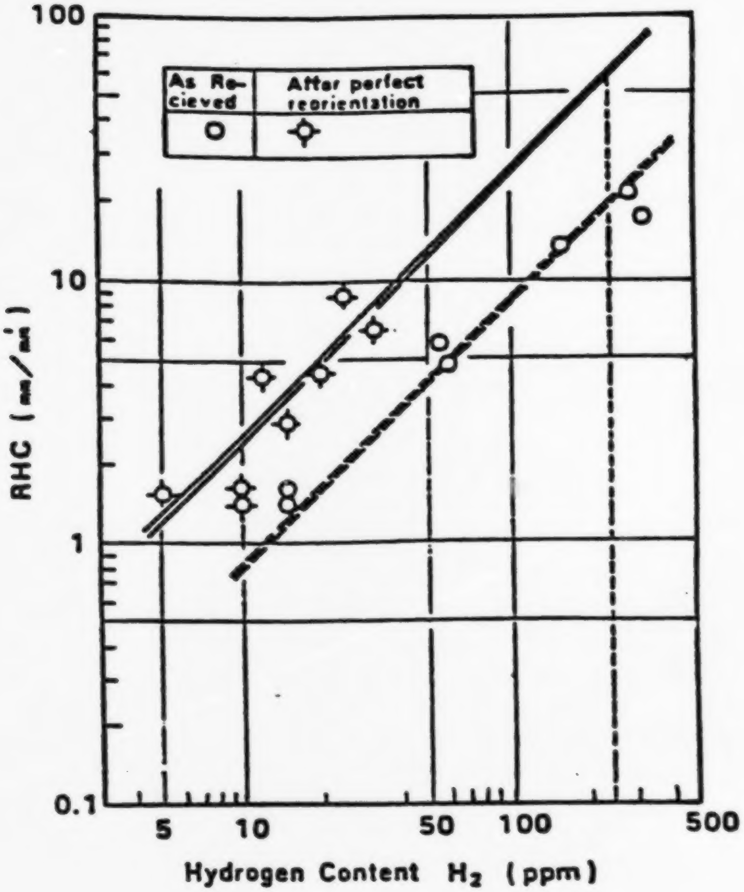


Figure 38: Relationship Between RHC and Hydrogen Content.
(Honda et al , ref.89)

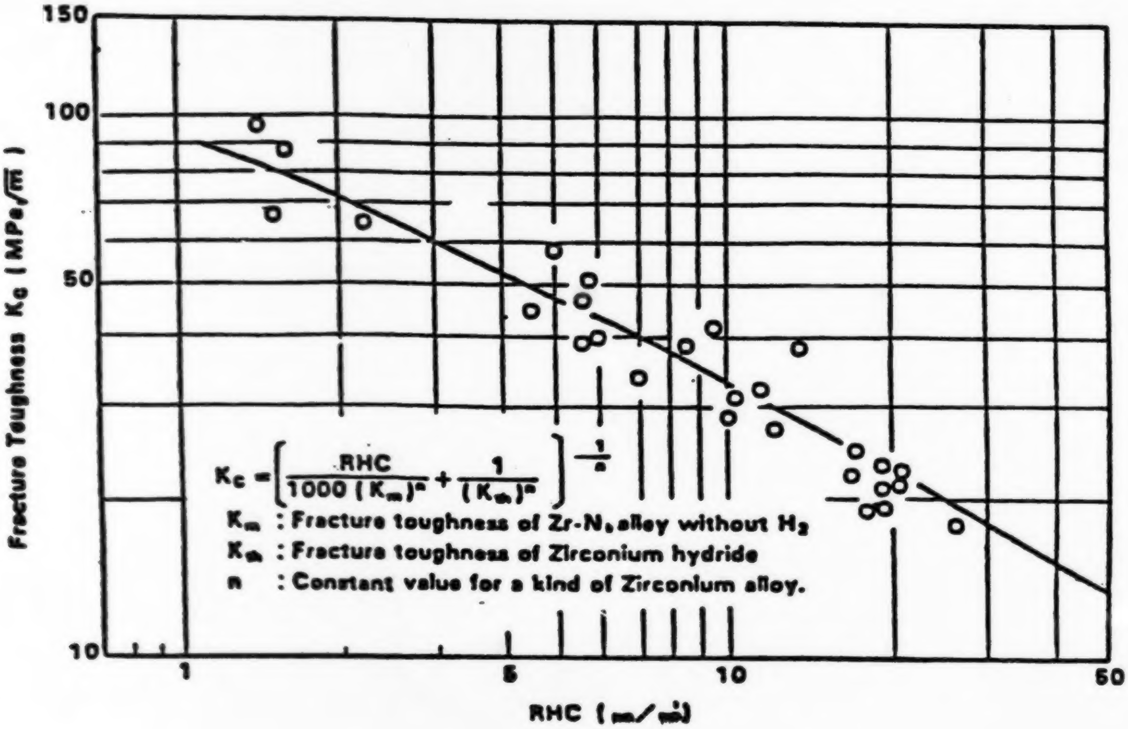


Figure 39: Effect of Hydride Reorientation on Fracture Toughness.
(Honda et al , ref.89)

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APPENDIX B

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